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CONTENTS

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THE SUBJECT of permeability of wood to liquids under pressure is of interest to the wood-preserving and pulp-making industries. Early students of the penetration of liquids into wood made use of methods similar to those used in commercial practice. Other workers, interested primarily in the problem of ascent of sap in trees, attached tubes to cut specimens of one or two years' growth and measured the rate at which the liquid entered the wood at constant head. More recent investigators, in order to determine more readily the influence of single factors, placed wood blocks or chips in suitable apparatus and determined the rate of flow in one direction. It was then found that the rate for continuous flow under constant pressure decreased with time, approaching equilibrium after about three hours. This decreasing rate of flow occurred quite generally although in some cases it was preceded by a period of increasing rate of flow.

Moreover, it was pointed out that a decreasing rate of flow of water under constant pressure was also quite generally encountered through filter media. Water shows decreasing rate of flow through filter paper or sand bed filters.

If, as seemed likely, the decreasing flow might be explained on the same basis in most cases, some more general explanation than, for instance, the pit aspiration theory for softwoods, had to be sought. Polar liquids penetrated wood slower than could be accounted for on a viscosity basis alone. There was evidence that electrokinetic properties of a liquid were also a factor in influencing its rate of flow through wood. On the basis of this evidence recent workers suggested that electrokinetic effects might likewise account for the decreasing rate of flow of liquids. No direct proof of the possibility, however, has been offered.

A few attempts, at least one of which was fairly successful on a small scale, had been made to increase the permeability of

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wood without seriously impairing its strength. Any method of maintaining the initial higher permeability might, of course, have some practical application. The first step in finding a method of maintaining the initial permeability of wood obviously is to discover the reason for the falling off in rate of flow.

To check the most commonly accepted theory, the electrokinetic mechanisms which might produce a decreasing flow were first considered. From electrokinetic considerations it is apparent that if the rate of flow fell off because of electrokinetic effects, the contact potential, ordinarily referred to as the "zeta" potential, should increase. Part I of this study is concerned with the electrokinetic changes occurring during continuous flow of water through wood. The zeta potential was measured by the streaming potential method. Although the results obtained in this study were negative in so far as they do not account directly for the decreasing rate of flow of liquids through wood, they are of interest inasmuch as they are the first quantitative measurements of streaming potentials on wood. Also for the first time an attempt has been made to determine, by a direct method, the electrokinetic potential for flow through pit membranes. Furthermore, these studies raised numerous questions concerning the effects of various variables affecting rate of flow and their possible relation to the decrease in the rate of flow.

The results of tests on a variety of woods and other porous materials are reported in Part II. The effects of various treatments, such as rapid alternation of direction of flow, also were determined. As in Part I, the aim of Part II is to accumulate data for use in developing a satisfactory explanation of the decreasing rate of flow of liquids through wood.

REVIEW OF LITERATURE

Although decreases in rate of flow of water through wood had been observed before 1900, it was not until very recent years that there was collected sufficient data to show decreases in rate of flow of a number of liquids through several species of wood. The scope of the investigations left no doubt that the rate of flow of liquids through softwood sections that had been soaked in the liquid tends to decrease.

Erickson, Schmitz, and Gortner (13) studied the rates of flow in a longitudinal direction of water, benzene, and 3 per cent zinc chloride solution through 14 softwoods and two hardwoods. In order to summarize the findings in their previous work with respect to the falling off in rates of flow, the writers calculated the final rates as percentages of the maximum rates. Benzene and zinc chloride on the whole showed the same proportionate decrease, to an average of 56 per cent of the maximum rate. The average for water, on the other hand, was a 72 per cent decrease, to 28 per cent of the maximum rate. The decreases through all groups of heartwoods were greater than through the corresponding groups of sapwoods. The rates of flow through non-resinous heartwoods decreased more over this period of time than did the rates through resinous heartwoods; in sapwoods there appeared to be less difference in this respect. The terms "resinous" and "non-resinous" as used here and elsewhere in this discussion refer to woods with and without resin canals, respectively. With the exception of the non-resinous sapwoods, through which the rate of flow of water decreased at a greater rate with the unseasoned sections of each species, seasoning appeared to have no appreciable effect on decreasing rate of flow.

The decrease in rate of flow through white oak sapwood was, no doubt, due at least in part to plugging by tyloses; that through birch sapwood, however, was especially puzzling, inasmuch as no apparent plugging or change in the dimensions of the path of flow could be observed. Unlike softwoods, the minimum dimensions in the path of liquid flow through paper birch (3μ between the bars of the perforation plates) are well within the microscopic range. Consequently, the peculiar behavior of this wood was an important factor pointing toward some general explanation for decreasing flow.

Later Erickson, Schmitz, and Gortner (14) determined the radial and tangential permeabilities of the same 16 woods. They found that penetration was from 10,000 to 400,000 times greater in the longitudinal direction than in the tangential direction in softwood sapwoods, while some resinous heartwoods and the two hardwood heartwoods were impermeable in the latter direction under the conditions used. Rates of flow in the radial direction varied from 40 to 6,000 times the rates in the tangential direction for different species of resinous woods. This difference was due to flow through the radial resin canals. In the non-resinous woods radial and tangential penetration were more nearly equal, with tangential penetration more often exceeding the radial. The decrease in rate of flow in these two directions appeared to be less than in longitudinal direction. However, this is probably not a real difference since a longer time was required for sections to reach the equilibrium rate under the conditions used when penetrated in the difficultly permeable directions; for, although higher pressures and thinner sections were employed, the pressure drop across each pit membrane was less, and flow was much less than in the longitudinal measurements. The rates after three hours were, therefore, further from the supposed equilibrium rates than those measured after a similar time of penetration in the longitudinal direction.

Erickson used two types of tangential sections: those composed of springwood only and those containing a maximum amount of summerwood. The writers have analyzed these data by the method previously described. If pit aspiration were a factor in decreasing flow, it might be expected that flow through springwood would decrease at a different rate than through summerwood because of the greater ease of aspiration of the pits of springwood. Of the eight comparisons possible, six had a somewhat greater decrease in rate through the summerwood, while two showed greater decreases in the springwood.

Buckman, Schmitz, and Gortner (7) investigated the flow of five organic liquids and water through wood sections brought to equilibrium with 95 per cent relative humidity (but not soaked in the liquid used before being run). They found that benzene, hexane, kerosene, bromobenzene, water, and nitrobenzene gave decreases in rate through balsam fir heartwood in the order named, with benzene and hexane decreasing to 84 per cent of the original, while nitrobenzene after 2.5 hours was flowing at only 19 per cent of its initial rate. Furthermore, the initial flow of nitrobenzene was abnormally low, being one fourth the rate of flow of water instead of one half as would be expected from viscosity considerations alone. It was suggested that this abnormally low rate might be due to electrical back pressure causing electroosmotic flow in the reverse direction. The decreases were in the order of increasing polarity of the liquids. Since swelling of wood also follows this order (42), it is likely that swelling was a factor, although not necessarily an important one. Erickson obtained similar decreases with the same woods when they were evacuated under benzene or water before penetration by these liquids.

Buckman, Schmitz, and Gortner also ran six salt solutions (0.1 N) through balsam fir heartwood sections which had previously been run to equilibrium with water. The initial rate with each salt solution differed markedly from the equilibrium rate with water, varying from 280 per cent with potassium chloride to 87 per cent with thorium chloride (0.01 N). With the exception of that for mercuric chloride solution, the rates all changed rapidly, approaching equilibrium after three hours. With zinc chloride the rate increased to 333 per cent of the rate with water, while the other four solutions gave decreasing flow. The final rate for zinc chloride solution was approximately 18 times that of the thorium chloride solution, yet their viscosities were not significantly different. When the salt solutions were washed out, the equilibrium rate with water was regained. While these decreases in rate of flow perhaps can be explained by a decrease in the effective pore sizes through swelling or oriented absorption, the initial rapid rates with most of the salt solutions and the increasing rate with zinc chloride are more difficult to interpret.

Buckman, Schmitz, and Gortner also investigated the relation between pressure and rate of flow of water through several woods. The rate was found to increase much more rapidly than the pressure for the non-resinous woods (eastern hemlock, northern white cedar, western red cedar, and balsam fir). With Norway pine sapwood the rate increased only slightly more rapidly than the pressure, while with white spruce sapwood rate and pressure were directly proportional.

Similar results for the heartwoods of black spruce and white spruce were found by Sutherland, Johnston, and Maass (57). To explain the nonlinear rate-pressure relation which they found for white pine, tamarack, Norway pine, balsam, and cedar heartwoods they postulated that the pit membranes stretched with pressure, resulting in an increase in size of the membrane pores.

The direct relationship in the case of spruce they thought was due to the fact that most of the pits of spruce heartwood are aspirated and therefore cannot be bulged. They also noted rapid decreases in rates of flow with time, with equilibrium being approached after three or four hours. If, after reaching equilibrium, the pressure were increased, constant flow at the new equilibrium rate would soon be attained. There was a slight lag in going back to a low pressure; this they attributed to a bulged condition of the membranes. As far as the time required to reach equilibrium was concerned, it made little difference whether the wood was presoaked with intermittent evacuation, unseasoned, or airdry at the start of penetration. Presoaking for more than 24 hours did not materially influence permeability. They state that the decreasing flow with time cannot be accounted for by pit aspiration or plugging by colloidal matter from the lumen. In two runs they reversed the direction of flow through the chips after they had reached equilibrium and found little change in rate. Despite their use of presoaked wood, they attributed the decrease to a further swelling of the wood, causing a decrease in size of the tracheid lumen and the pit membrane pores. They also believed the Jamin chain effect might have influenced flow through wood.

Johnston and Maass (24) also reported decreasing rates of flow of water and sulfite solutions through wood chips. Scarth (43) noted a curious behavior of sapwood upon reversal of direction of flow. He states, as quoted by Gibbs (17): "When water is forced by ordinary tap pressure in a longitudinal direction through a block, a very rapid initial flow is obtained which falls off after a few minutes. When direction of flow is reversed, it is again rapid, and once more falls away. This might be due to torus action or blockage of the pores of some sort."

Ewart (16) observed that the permeability to water decreased upon death of hardwood twigs. The rate of flow through cut stems decreased with time. While trimming the ends under water increased the permeability beyond what would be expected, the original rate of flow was not regained. To simulate a wood vessel, he trapped air in a fine glass capillary of irregular bore and found that rates of flow down or in the horizontal direction were about equal, but rate of flow up was much slower. He cites several other workers who found similar decrease in flow with hardwood stems.

Compiling the literature relating to the problem of decreasing flow through woods involves more than merely pointing out the several studies on wood in which the phenomenon has been observed. The review must be extended to include flow through other porous materials, especially those which also give decreasing flow. Since flow through softwoods is essentially governed by the resistance to flow offered by pores of submicroscopic size, the general problem of flow of fluids through extremely fine capillaries, a subject which one cannot say is thoroughly understood, is also involved. Such factors as the so-called "increased viscosity of water in fine pores" might enter in. Since workers both on wood and cellophane have suggested that the decreases have an electrical origin, the field of electrokinetics must be touched upon, particularly with respect to streaming potentials in fine capillaries. Wood penetration is also intimately connected with wood structure, and the streaming potentials are dependent on the nature of the surface of the woody parts in the path of flow. Swelling of wood, a factor which was early blamed for decreases in flow, will also be considered.

Bigelow (2) found the rate of flow of water through collodion and unglazed porcelain membranes to be essentially constant, but for parchment paper it decreased with time. In one run the rate after 80 minutes was 15.8 per cent of that at 13.5 minutes. In another run, in which the rate had dropped to one half the initial value, the original rate was regained after standing two hours with no flow. He found that, after the rate had decreased to low values, it could be increased considerably by increasing the pressure for a time and then returning to the previous pressure, but the new rate was still only one third of the original rate. He states that "the regularity with which the permeability falls off, and the fact that the falling off is far greater than anything observed with any other material, makes it highly improbable that the phenomenon is due to mechanical stoppage of the pores by solid particles."

He found the rate to be almost directly proportional to the pressure through collodion, gold beater's skin, and unglazed porcelain, but the rate increased faster than the pressure through parchment. When the pressure was increased 1.9 times the rate increased 4.7 times. This is similar to the behavior of nonresinous woods; Buckman, Schmitz, and Gortner (7) found that doubling the pressure on seasoned northern white cedar heartwood increased the rate by 4.3 times, while with unseasoned balsam fir heartwood it increased 6.2 times.

Ruth (41), using quartz particles packed in a tube, found that the rate of flow decreased with time when water flowed through, but remained constant when ethyl alcohol was used.

Schafer and Carpenter (45) sought to use the rate at which flow of water decreased through groundwood as a means of characterizing or evaluating the pulp. They devised an equation for the decreasing flow.

Hisey and Heigl (20) applied Ruth's theoretical analysis of filtration operation to drainage of a pulp suspension through a forming mat of papermaking fibers. Their runs were made at constant rate, the pressure drop across the sheet being recorded automatically. With an unbeaten pulp the specific resistance seemed independent of the pressure drop; with slower pulps it appeared to increase as the pressure drop increased. They postulated a compression of the fiber mat by the higher pressures, thus reducing pore size, and suggested that their method might be used for the determination of the compressibility of pulp fibers. Their results, however, directly contradict the findings of other workers who report that the rate of flow increases faster than the pressure for fibrous materials. Probably the explanation lies in the fact that Hisey and Heigl made their runs with white water in order to approach mill conditions. Data were not collected until a balanced condition was attained so that the fines lost from the pulp in the process of sheet making were made up by the fines introduced in the white water. They seem to have neglected to take into account the probability that the fines which pass through do so toward the beginning of sheet formation; later an increasing number are trapped in the pores and increase the resistance out of proportion to the increase in sheet weight.

Bishop, Urban, and White (3) list several workers who have noticed "blocking effects" or decreasing permeability of membranes. In their own studies on cellophane they found rapid decreases in rate of filtration and electroosmosis to as low as 10 per cent of the initial rate after 15 to 60 minutes. Addition of salts to the water decreased the blocking effects. Blocking disappeared when 0.01 g. $ThCl_4$ per liter was used. With pressure alone, when the pressure was removed, a back flow in the reverse direction resulted, continuing for several minutes. If the pressure were merely reduced to a relatively low value, flow would at first reverse but later proceed in the original direction. The same applied to application of current alone without pressure, indicating that stretch of the membrane was not a factor. Upon cessation of applied current, a residual (polarization) E M F persisted, and its disappearance had a course closely paralleling that of the accompanying filtration. It thus appeared that the blocking of filtration through these membranes might be correlated with the electrical phenomena of the nature of polarization which are associated with electroendosmose. They explain the absence of measurable streaming potential through cellophane as being due to a discharge through relatively inactive smaller pores, through which the potential is built up slower and flow retarded by electroendosmose in the opposite direction. It is to the latter effect that they attribute the falling off in rate of flow.

Erbe (12) doubts whether the blocking observed by the above workers can be explained by a streaming potential. He cites Simon and Neth, who showed through a series of experiments that electroosmosis was not a factor in blocking. They also found that water and various other liquids had a constant rate of flow through fine glass, porcelain, or collodion filters if the liquids were previously filtered shortly before use. Either standing 20 to 30 hours or boiling resulted in decreasing flow. Erbe states that theoretically it can be shown that "blocking through streaming potential can always be only very small, and indeed can practically always be neglected." His calculation shows this to be true for water through a capillary of 1 μ diameter.

Erbe found that single distilled water gave decreasing flow through a "Membranefilter," but that double distilled water gave constant rate. His data show only a slight tendency for KCl to flow faster than water. Many observers (cf. Steiner, [56]; DuBois and Roberts [11], and Ruth [private communication]), however, have found that the addition of an electrolyte increases the rate above that of water in filtration through a membrane or filter media. In the experiments of Steiner (56) in the filtration of "clay suspensions," it was found that if the suspension were made up in 0.2 per cent $FeCl_3$ solution, twice the volume of filtrate would be collected in three minutes than when water alone was used. Brukner and Manegold and Hofmann explain changes in permeability by changes in the thickness of adsorbed water dipoles.

White, Monaghan, and Urban (60) have outlined clearly the two mechanisms by which decreasing flow may arise from electrokinetic changes. The variations in rate of flow which they found with increasing concentrations of $ThCl_4$ fit in well with the electrokinetic theory. The rate reached a maximum at the isoelectric point (at which the double layer thickness is a minimum), $4x10^{-5}$ M, averaging 5 per cent higher than the rate with water. On further additions of $ThCl_4$ the rate decreased, reaching a minimum of $4x10^{-3}$ M, when it was about 22 per cent lower than at the isoelectric point. Further additions increased the rate, but above $1x10^{-1}$ M the rate again fell off, this time due to mechanical blocking by adsorbed thorium hydroxide. They found electrokinetic potential and filtration rate to be inversely proportional. The rate was proportional to pressure and gave constant flow; the previous rate with water could be regained by washing out the $ThCl_4$. They calculated roughly that the double layer thickness for isoelectric $ThCl_4$ was of the order of 56 mμ, very much greater than the largest pores of cellophane "600" (2-3 mμ), and that consequently the double layer was very much compressed in the pores. They demonstrate diagrammatically how the "zeta potential for a small-pored membrane will be greatly reduced from the normal value because of the necessarily compressed state of the diffuse layer."

White, Urban, and Strassner (61) give a brief description of Stern's conception of the double layer. For the thickness of the double layer on pyrex glass particles they calculated 55 mμ for

1.25×10^{-4} molar, 39 mμ for 2.5×10^{-4} molar, and 2 mμ for 1×10^{-1} molar KCl.

Bull and Moyer (10) summarized the observations of other workers on the decrease in streaming potential in small capillaries. They use the term "critical radius" for the radius of a pore below which the calculated zeta potential will be more than 10 per cent too low. In experimenting with cellulose diaphragms they found the average radius of the pores to be about 0.9 μ, which is above the calculated critical radius when solutions of mono-monovalent electrolytes of a concentration of 10^{-4} N or greater are used. They state, however, that a large number of pores were undoubtedly below the critical range, and therefore it is difficult to determine the true potential in such cases. Furthermore, they believed that measurements made much below a capillary radius of 0.1 μ are likely to be in error because of the "increase in the viscosity of water produced by small pore diameters."

Wilsdon, Bonnell, and Nottage (62) find that "a growing mass of evidence points to the necessity of assuming a modification in properties of liquid films in porous materials, even in thicknesses corresponding with many molecular layers."

Wolkowa (63) found constant values for calculated pore radii of packed powder diaphragms when penetrated by nonpolar liquids such as benzol or carbon tetrachloride. Polar liquids, particularly water, gave smaller values.

In his experiments on clays, Terzaghi (58) was led to the conclusion that the viscosity of water in very narrow flow sections is enormously greater than the viscosity of free water, varying inversely with the eighth power of the slit width. Using the equation which he developed, he calculated the viscosity of water in a slit 36 mμ wide to be between 10,000 and 16,000 times normal.

It is interesting to note that when Quinke (38) in 1859 made the first observations of streaming potentials, wood sections and groundwood diaphragms were among the materials he used to show qualitatively that potentials arose. Because of the difficulties encountered, Quinke soon abandoned the use of wood. No further electrokinetic studies on wood were reported until 1926 when Stamm (47) made quantitative measurements of the zeta potential of several species. After drilling fine holes in the tangential and radial sections of heartwood of Sitka spruce, Alaska cedar, western red cedar, western hemlock, and Douglas fir, he measured the velocity of electroosmosis when a potential was applied across the wood membrane. Knowing the capillary cross section from the number and diameter of the holes drilled, he was able to calculate the zeta potential to be between 13 and 14 millivolts, a value comparable with that found for cellulose by various workers. He next used cross sections of wood thin enough so that most of the tracheids were cut twice, thereby forming open passages across the wood so that no pit membranes had to be traversed. Using the average value of 13.6 millivolts found for zeta, he calculated the effective cross section for the wood membrane from electroosmotic data. This involved the assumption that the zeta potential previously calculated for the wood as a whole also held for the inner walls of the tracheids, which alone would determine the zeta potential in the latter case. This assumption was reasonable because the secondary wall forms the large part of the wood substances, and was justified by the fact that the cross section calculated by this method checked closely with that calculated from microscopic measurements. In a similar experiment on tangential sections in which practically all the penetration was through the twice-cut cells of the wood rays, the calculated area of the ray cell lumens agreed closely with that found from photomicrographs.

To calculate the pit membrane pore radii from electroosmotic data, Stamm made the assumption that the potential of the membrane is also 13.6 millivolts. (Pit membranes, however, constitute but a small portion of the total wood substance. Furthermore, there is considerable evidence [17, 22, 25, and 40] that these structures differ chemically from wood *en masse*. Consequently Stamm's assumption seems hazardous.) Knowing the velocity of electroosmosis through open tracheids he could then use a proportionality between the electroosmotic velocities and the cross sections in order to calculate the fractional effective pit membrane pore cross section when wood diaphragms longer than one maximum fiber length were used. These data combined with pressure permeability gave pit membrane pore radii ranging from 11 to 23 mμ for several softwoods (50). These values are of the order found by other investigators for various natural and synthetic membranes. Moreover, that they are approximately in the correct range is evidenced by determinations by four independent methods: (1) Penetration with mercury sol of 8 μ particle size. Some particles pass through; most are retained. (2) Electrical conductivity of KCl solutions in the wood. (3) Minimum pressure required for the penetration of air through the wood soaked with water or other liquid of known surface tension. Calculation from Jurin's law gives the maximum pore size. (4) Rate of change of velocity of flow of air with changes in the effective capillary radius, which varies with moisture content or relative humidity. This method, although it does not permit great accuracy, enables the plotting of the entire size distribution of the pores.

Fairly close agreement is obtained in results by these different methods which Stamm devised and applied (48, 49, 50, and 51). The assumption that when the wood is filled with KCl solution the conductivity of the cell walls is negligible compared with conductivity through the capillary structure was later found to be invalid (55). Results obtained by the conductivity method are consequently too high; nevertheless, they check quite closely with results by the electroosmotic method.

Unfortunately the only complete results reported for the last method listed, which involves flow of air of various relative humidities through wood sections seasoned to equilibrium with various moisture contents, were reported for a species on which no measurements of average effective radii by other methods have been reported. Stamm's results for white pine heartwood are as follows (54):

Section	Effective pore radii Millimicrons			No. of pit membranes traversed in series
	Minimum	Average	Maximum	
Longitudinal	10	36.5	5000*	4
Tangential or radial	10	28.5	74	30

* Apparently a few resin canals were open for longitudinal penetration.

In these experiments Stamm noted a decrease in rate of flow of the air through the wood. "The pressure drop ratios built up to a maximum and then decreased to an equilibrium value which was used in these calculations. This effect for vapor flow was considerably less than reported by Buckman, Schmitz, and Gortner for liquid flow, as might be expected, for electrokinetic effects would undoubtedly be less for vapor flow than for liquid flow."

By following the particles in an ultramicroscope, Lottermoser (30) measured the electrophoretic mobility of "cement" pulp (which he defined as that part of a suspension of groundwood which did not settle out in three weeks' standing). He found that a cement pulp sol was flocculated easier than a lignin sol, but less easily than a cellulose sol, by the chlorides of Na, K, Mg, Ca, Ba, Al, La, and H. With $ThCl_4$ an irregular series was obtained.

It has been known for some time that there are electrical currents flowing in definite directions through many living plants. Lund (31) has done an extensive amount of work on Douglas fir, in which he finds a continuous current in the living parts of the wood. By comparison with Stamm's results he finds that the polarity is in the right direction to explain transport of water upward in the wood. However, his experiments in applying a potential to the wood and measuring electroosmotic flow are not conclusive. He suggests that the function of the current is to produce electroosmotic flow of sap.

Marinesco (32), on the other hand, regards potentials in plant stems as the result rather than the cause of sap flow. He showed that greater transpiration gave higher potentials; but with some plants rate and even direction of flow could be altered by the application of a potential.

The question has frequently been raised as to the equivalence of the three common methods of measuring the zeta potential. For instance, Monaghan, White, and Urban (33) found different isoelectric concentrations for electroosmosis and streaming potential at a glass interface. Moyer (35) has recently reviewed electrokinetic theory in this connection and summed up the results of various workers who used different methods on the same materials. He concludes that the three methods yield identical results for uncoated similar surfaces in electrolytes of sufficient ionic strength, or for protein coated surfaces with or without electrolytes. For uncoated surfaces, however, such as cellophane or quartz with pores below the critical radius the evidence at present is against the equivalence of these methods as calculated by the usual equations. These discrepancies are also predicted by theory.

The data of various investigators indicate that with substances which show decreasing rate for conditions of viscous flow, the rate "increases faster than the pressure." Some other materials which show the latter phenomenon will therefore be included in this discussion. There is evidence that white spruce and Norway pine sapwoods, for which a nearly linear rate-pressure relation has been reported, also give almost constant rate of flow. Many exceptions for the two woods have been reported, but the measurements were not made on the same sample or on matched samples.

King (26) experimented with the flow of water and other fluids through sands, sandstones, and packed brass wire gauze. In all cases in which his velocities were low enough to insure viscous flow, he found that the rate increased faster than the pressure. Rate of flow through most of his sandstones fell off with time. He found that use of water from which the air had been removed had no appreciable effect on the rate-pressure relation. King (26) and Underwood (59) list numerous other workers whose data show this same deviation from Poiseuille's law.

Hinchley, Ure, and Clarke (19) showed that the rate of flow through a textile cloth is approximately proportional to the square of the pressure. Underwood (59) admits that the physical interpretation of this relation is not clear. His explanation is based upon a conception of cloth as a number of small orifices bounded by compressible fibers, with the diameter of the larger channels increasing at higher rates of flow at the expense of the smaller channels. But no physical basis for an increase in diameter of the larger capillaries is offered. Another explanation, suggested by Pickard (as quoted by Underwood), is that "the cloth consists of a number of short tubes partly blocked by fibers branching across them. As flow increases these fibers are swept aside and the resistance to flow is reduced."

Johnston (23) once believed that rate of increase of flow with pressure followed the formula for turbulent flow in pipes. Later Johnston and Maass (24) found turbulence to be of relatively small importance. They found that rate increased faster than the pressure in flow of air through jack pine heartwood.

In examining existing data on rate-pressure relationships in wood, the power of the pressure required for a direct variation with the rate was calculated from the equation:

$$\frac{R_1}{R_2}=\left(\frac{P_1}{P_2}\right)^n \quad \text{or} \quad n=\frac{\log\frac{R_1}{R_2}}{\log\frac{P_1}{P_2}}$$

The values for n, henceforth referred to as "pressure exponents," for increasing pressures, calculated from the data of Buckman, Schmitz, and Gortner (7) varied from 2.00 to 3.03 for unseasoned non-resinous heartwoods, while those calculated from the data of Sutherland, Johnston, and Maass (57) for various woods and pressures varied from 1.06 to 7.6.[3] The exponents exhibited fair agreement for different samples of the same wood run by the same investigator. For the non-resinous woods, with the excep-

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[3] See footnote 4 on page 28.

tion of the balsam fir run by Sutherland, the exponent remained quite constant over the pressure range investigated. Generally, for other woods the exponents decreased with increasing pressure. With five of the sections reported, increasing exponents were found in increasing the pressure in the high pressure ranges; this may be evidence of something of the nature of a rupture of the pit membrane.

The workers at McGill University (24), (57) generally favor swelling as the cause of decreasing flow, but have offered no proof. Koehler (27) observed that either boiling or leaching in cold water increased the subsequent shrinkage of redwood on drying; the dry, leached wood swelled more than a similar unleached sample when resoaked. Stamm (53) and Schwalbe and Beiser (46) found that no swelling into the lumen of wood occurred. Saechtling and Zocher (42) found swelling of wood in benzene, ethyl ether, methyl acetate, methyl alcohol, and water to be in the order of their dielectric constants. Stamm (55) pointed out that if benzene and its homologs be arranged in the order of increasing volumetric swelling of white pine in these liquids, this order is close to the same as that for their dipole moments or negative zeta potentials on cellulose. However, if his swelling data for the fatty acids and the simple aliphatic alcohols be compared with recent data as to the electrical properties of these liquids, no parallelism appears, except that with the fatty acids swelling rather tends to decrease with increasing dipole moment or negative zeta potential.

This review will not cover the numerous impregnation studies because they have been adequately summarized elsewhere (7), (13). Of the work done in establishing the paths of penetration in woods, only that of I. W. Bailey (1), who first demonstrated that bordered pits function in wood penetration, will be mentioned. His photomicrographs of woods penetrated by carbon suspensions (much of which passed through) revealed carbon deposited in the pit membrane in a rim about the torus and in lines radiating out from it. In an untreated section of larch he photographed a similar arrangement of radiating lines. Some investigators regard the lines as formed by areas of different thickness rather than as relatively open slits.

The possibility of commercial application of electroosmosis to wood preservation has been considered by Perruche (36). Also Stamm's successful attempts (52) at increasing the permeability of wood by chemical means may prove of practical import. With Sitka spruce penetration by chlorine gas in the longitudinal direction for two hours, followed by steam for one-half hour, increased the rate of flow with water by thirty times, while strength of the wood was reduced only slightly. With Douglas fir the observed permeability increases were only of the order of five times, although more drastic treatments were used. Attempts to rupture the pit membranes by suddenly releasing the pressure on a partially water soaked section were unsuccessful. Scarth and Spier (44), and Sutherland, Johnston, and Maass (57) reported increased permeability after treatment with boiling water or pulping solutions.

Chip separation by vacuum tank flotation of the heartwood is an example of commercial utilization of differences in permeability of different parts of the same wood. Another possible relation of wood penetration studies to the sulfite process was brought out by the work of Morgan and Dixson (34), who found that the use of high initial pressures gave a marked improvement in all cases. This would be expected if the time required to reach equilibrium rate were independent of the pressure used.

PART I

ELECTROKINETICS AND WOOD PENETRATION

APPARATUS AND METHODS

The woods used for the electrokinetic experiments were from the same supply as that used by Erickson, Schmitz, and Gortner (13) in their studies of longitudinal permeability. These woods had been seasoned under conditions of gradually decreasing humidity at 30° C., cut into sections measuring one centimeter in the longitudinal direction, and stored in sealed jars. In preparing the samples for use they were prehumidified by standing over 16 hours in a desiccator containing free water. They were then immersed in the liquid used and evacuated for a total time of at least 30 minutes distributed in three periods. Although a slight amount of air still remained in the wood soaked in this manner, further evacuation did not appear to have an effect on the curve of continuous flow.

Small cylindrical samples were cut from the wood blocks, using a cork borer or sharpened brass pipe having a diameter just under 1.7 cm., and inserted in a thick glass cylinder 1.7 cm. in diameter. Dental rubber dam (heavy grade) was stretched between the glass and the wood to form a water-tight packing when the tension on the rubber was released. The glass cylinder was 0.8 cm. long, so that the wood protruded 0.1 cm. from each end. A rubber gasket which could be compressed almost to 0.1 cm. thickness was placed around the ends of the wood. Next perforated gold electrodes with spot welded platinum connecting wires were placed over the ends of the wood, followed by another set of rubber gaskets. The four gaskets were held in alignment by two glass rods passing through the outer portion. The cell was then clamped together vertically between two heavy glass flanges which tapered down to regular tubing size. This cell was similar to that used by Briggs (5).

As containers for the supply liquid, two one-gallon glass bottles were used in series. Preliminary experiments had shown that dissolved air in the liquid might have an effect on the rate of flow curve; also, Lauffer (28) had found that to get constant results by the streaming potential method the water had to be caught directly from the still and cooled out of contact with air. In the present experiments the air was removed from the liquid by boiling at room temperature by drawing a vacuum. A small amount of air probably remained held in solution by the hydrostatic head of the liquid. When only about half a liter remained in the bottle to which the air pressure was applied, it would be refilled and a vacuum again drawn on both bottles. No air bubbles were noticed arising from the second bottle so the system was adequate protection against dissolved air.

A tank of 5 cubic feet capacity, filled from the laboratory air line, was used as a source of pressure. The electrical circuit used in measuring streaming potential and cell conductivity was the same as that used by Lauffer (28). Conductivity of the liquids in the diaphragm was measured by the Wheatstone bridge method using 110 volt A.C. The 0.1 N KCl for determining the cell constant was contained in a separate bottle (connected by a T tube to the tube beneath the cell) upon which pressure could be applied to stream 300 cc. of KCl through the wood. With further streaming the conductivity did not change greatly. The cell together with the supply bottles and KCl were kept at 30° ± 0.5° C. in an air bath.

Rate of flow was measured by determining the time for the liquid to fall vertically into Mohr pipettes of 1 or 10 cc. capacity. The liquid fell into the pipette from a T tube which had its upper arm open to the atmosphere. The hortizontal arm of the T tube could be adjusted to the level of the liquid in the supply bottle.

Connections for reversing the direction of flow through the cell without removing the cell were included.

After the cell was clamped in the apparatus, it was inverted and bubbles of air which were sometimes trapped beneath the wood were run out through an exit tube below the wood. When the cell was replaced in position the liquid was started streaming through the wood and the initial rate was measured. A series of measurements of the conductivity of the diaphragm was then made. This conductivity decreased very rapidly during the first several minutes of a run using wood. For calculating the zeta potential, the conductivity at the time of measurement of the streaming potential must be known. Since the two could not be measured at the same time, it was necessary to extrapolate from a series of conductivity measurements in order to estimate the conductivity at the time when the first streaming potential was measured. Zeta potentials were calculated using the cell constant determined at the end of the run.

For electrokinetic runs using cellulose, Schleicher and Schüll white ribbon filter paper No. 589 was used. It was prepared by the method used by Lauffer: pulped in alcohol, dried in vacuo, and stored in an air-tight container. Two batches were made, the first pulped in a ball mill, the second in a glass jar using an electric stirrer with glass mixing rod. Before using the cellulose it was pulped in the liquid to be used and allowed to stand at least a week with occasional agitation. The cellulose diaphragm was then formed by holding the glass cell over one electrode on the suction flask, pouring in a cellulose suspension, and tamping the cellulose down with a glass rod.

The equation given by Briggs (5) for the calculation of zeta potential by the streaming method is:

$$\zeta = \frac{K_s H}{P} \cdot \frac{4 \pi \eta}{\epsilon} .$$

When water having a viscosity of 0.01 poise and a dielectric constant of 80 is used, the equation becomes:

$$\zeta = \frac{H K_s}{P} \times 1.0596 \times 10^2$$

where H is the streaming potential in millivolts, P is the pressure in centimeters of mercury, K_s is the conductivity in reciprocal ohms, and ζ the potential difference across the double layer in volts.

Based on this equation, the working formula for calculating the zeta potential at a pressure of 20 pounds per square inch is:

$$\zeta = .01441\ C\,H\ .\ \frac{B}{A\,R}$$

where C = resistance with KCl streaming through the diaphragm,

$\frac{B}{A\,R}$ = resistance with water streaming through the diaphragm,

$\frac{B}{A}$ = ratio of the two arms of the Wheatstone bridge, and R = resistance of resistance box.

ELECTROKINETICS AND DECREASING RATE OF FLOW

Electrokinetic theory offers two mechanisms of decreasing flow: (1) Increase in thickness of the electrokinetic double layer, thus decreasing the effective size of the capillaries, and (2) Increasing electroosmotic flow in the reverse direction.

1. δ, the thickness of the double layer, is given by:

$$\delta = \frac{\zeta\ \epsilon}{4\,\pi\,e}$$

where ζ is the potential difference across the double layer, ϵ is the dielectric constant, and e is the charge per unit area.

It has been pointed out, however, that this equation does not hold for the case where the thickness of the double layer is appreciable compared with the width of the capillary. Since the mechanism does involve a double layer of appreciable size, the formula given would not hold if it were a factor. However, for the present purpose—that of determining whether the zeta potential of wood changes with time, and whether that change is in the direction which might account for the decrease in rate of flow—the equation as given above was considered adequate for comparative purposes. Furthermore, because of the uncertainty of value of the dielectric constant of the liquid as it exists in the double layer, even the values of the zeta potential as ordinarily calculated for large capillaries may not have an absolute physical significance.

From the foregoing formula, it can be seen that if δ is to increase, either ζ must also increase or e must decrease. An indication of whether δ does change might be obtained by the measurement of these quantities. ζ, the zeta potential, can be calculated from the streaming potential.

Gouy calculated the thickness of the diffuse double layer to be of the order of 1 mμ for 0.1 normal NaCl, 10 mμ for 0.001 normal NaCl, and 1,000 mμ for conductivity water. The latter figures are of the order of the diameters of the submicroscopic pores of the pit membrane. Since electrolytes reduce the thickness of the double layer, the thickness will increase as the wood is leached. But the size of the double layer also depends on the nature of the surface, which may change with flow. For instance, a soluble coating might be removed from the resisting surfaces, uncovering a substance having a greater attractive force for the hydroxyl ions of water thus increasing the thickness of the double layer and reducing the effective capillary dimensions. An increase in zeta potential as flow decreases would indicate such a change.

2. The other possibility, an increasing electroosmotic flow in the reverse direction, would be produced by either an increasing streaming potential or increasing zeta potential, according to the expression:

$$V = \frac{Q \zeta H \epsilon}{4 \pi \eta l}$$

where V is the volume of flow, Q is the total capillary cross section, l is the effective capillary length, and H is the potential across the membrane (in this case it is the streaming potential). From this equation it is seen that if flow is to decrease due to electroosmosis, then to produce an increase in volume of flow, V, in the reverse direction, either the zeta potential, ζ, or the streaming potential, H, must increase. Since $\zeta \propto H$ and $V \propto H \times \zeta$, V is $\propto (\zeta)^2$.

If either mechanism were a factor in producing the decreasing rate of flow, it would therefore be expected that the zeta potential would increase as the rate of flow decreased.

The zeta potential, representing the absolute electrical potential at the interface, is independent of the area of cross section or length of the capillaries in the diaphragm. The potential is, however, characteristic of the diaphragm material, even varying when cellulose from different sources is used to make up the diaphragms. When wood is used as a diaphragm, the potential which is set up may be regarded as the sum of the potentials arising from surfaces which may be of a different character.

STRUCTURAL FACTORS IN RESISTANCE TO FLOW THROUGH WOODS

In the case of most hardwoods, penetration takes place largely through the vessels. Many hardwoods have their vessels partially occluded with tyloses, and these structures together with the walls of the vessels will determine the zeta potential. However, in the case of paper birch (through which the flow is often less than 10 per cent of the initial after 3 hours), the vessels are supposedly free from tyloses. Vessels are built up of a series of vessel segments joined end to end to form a more or less uninterrupted tube. In the case of birch the opening between adjoining segments is crossed by bars of cell wall substance, forming what are called scalariform perforations. It is at these perforation plates that much of the resistance to flow of liquids through birch must occur, although it is not apparent why flow should decrease through what under the microscope appear to be open tubes, with minimum openings of about 3 μ which are readily visible at the perforation plates. The zeta potential calculated from streaming potential measurements through birch should be characteristic of the substance composing the bars of the perforation plates or any substance accumulating on them.

Some potentials were measured on white oak sapwood and on paper birch, but most of the electrokinetic studies were on softwoods. The important factor in determining the zeta potential of softwoods of sections greater than one tracheid length is the pit membrane connecting adjoining fibers. In the third stage of the development of the cell, namely, cell wall thickening, the secondary cell wall is not deposited uniformly over the entire inner surface of the cell, but thin spaces are left which are known as "pits." Complementary pits generally form opposite in the wall of the adjacent cell, resulting in "pit pairs." The pits of a pit pair remain separated by the compound middle lamella which is made up of the primary walls of the two contiguous cells together with the intercellular substance.

Bixler (4), by digestion with pulping solutions, found that the intercellular substance of spruce is largely lignin, the primary wall largely cellulose, the outer secondary wall next to it largely lignin, while the inner secondary wall is largely cellulose. This verified Kerr and I. W. Bailey's picture of the cell wall (25). Ritter, Lewis, A. J. Bailey, and others have found evidence that laterally wrapped fibrils are an important structural part of the primary wall.

Although the pit membrane is merely a specialized part of the compound middle lamella adapted for transporting liquids, it does not necessarily follow that it has the same chemical composition. Jeffrey (22) states that while the cement substance (middle lamella) uniting the cells is in general lignified, "in the region of the pit membranes the middle lamella becomes pectic cellulose, and here water passes through the walls much more readily than it does elsewhere."

Evidence for such a difference was found by Gibbs (17) in his photomicrographs of the residues of spruce sections which had been extracted with lactic acid—hydrochloric acid, followed by treatment with 72 per cent sulfuric acid. Only the tori, in many cases the pit membranes, and in some cases the arched "borders" of the pits remained intact. Some of the pits had therefore retained their original appearance while almost all of the remainder of the wood had been dissolved away. Where only a torus and part of a pit membrane remained, the edges of the membrane presented a rather regular raggedness, which might correspond to pores. Gibbs thought that in a few cases he could discern the pores of the membrane as elongated radiating areas.

Ritter (40) claimed that microscopic examination of the middle lamella lignin indicated that the "inner surface of the chamber wall of bordered pits is lined except at the pit orifice with a thin membrane of lignin (an extension of the middle lamella), over which is a thickened covering of lignified cellulose (an extension of the cell wall). Moreover, the pit membrane with its thickened portion, the torus, . . . is composed of lignin."

In non-resinous softwoods most of the resistance to flow will arise at the pit membranes. The pressure drop through the wood is the sum of the head loss caused by the friction of the fluid in viscous flow through the cell lumen and the pit perforations, plus the frictional effects due to eddy currents set up around the pits. Hawley (18) and Stamm (54) have shown that the latter effect, generally referred to as "impact turbulence," is of minor importance.

Calculations of Reynold's number show that even in the largest hardwood vessels flow was laminar at the highest pressure used. For turbulent flow or flow through orifices (impact turbulence) the rate varies as the square root of the pressure drop. The impact turbulence as the liquid enters the wood and the kinetic energy correction for the liquid leaving are negligible.

In resinous woods it has been shown (15) that the resin canals may play a part in the conduction of liquids forced through wood under pressure, but what proportion of the flow is through the resin canals is generally not known for penetration in the longitudinal direction. No doubt it varies with the species and depends also on the thickness of the section and the pressure used. Thus in resinous woods there will be this additional surface involved in the setting up of the electrokinetic potential.

In the present study, streaming potential measurements on transverse sections of wood 1 cm. thick were used for calculation of the zeta potential. The streaming liquid had to traverse at least one, and in most cases several, pit membranes. The woods used were largely sapwoods whose permeability had been determined by Erickson, Schmitz, and Gortner (13), using 5 cm. of mercury pressure. In order to get significant streaming potentials, the same woods were now run at 20 pounds per square inch. Heartwoods are less suitable for streaming potential measurements because of their higher electrical conductivities. Also they have infiltration substances as an added variable.

DISCUSSION OF RESULTS

The streaming potentials set up in longitudinal flow through various heartwood sections 1 cm. thick at 20 pounds per square inch pressure were found to range between 5 and 15 millivolts. For non-resinous sapwoods under similar conditions the streaming potentials were of the order of 100 millivolts. Table 1 is a summary of the zeta potentials calculated from streaming potential measurements. Several unmatched samples of the same non-resinous woods were run to find out to what extent the potential might be characteristic of the species. For the final potentials the agreement is poor. For the initial potentials there seems to be quite good agreement, with the exception of runs 17 and 18 in which the cell constant was measured immediately after these first potentials were measured.

As has been pointed out, the values reported here for zeta are, for softwoods at least, not absolute determinations of the contact potential. This is because the pores of the pit membranes are below the critical radius for which the common streaming potential equation holds. The equation was used, nevertheless, for through it streaming potentials can be reduced to a more comparable basis. Potentials during a run can then be plotted as a function of time since the changing conductivity of the diaphragm is taken into account by the equation. Furthermore, the use of the cell constant in the calculation makes different samples of the same wood directly comparable, and different species may then be compared on somewhat the same basis also.

In pores below the critical radius the double layer is compressed, so that its thickness is less than when unrestricted. The smaller the pore, the thinner the double layer. The zeta potential as calculated by the usual equation is directly proportional to the thickness of this double layer. Therefore the apparent zeta potential calculated in this manner is lower than the actual contact potential. Were a quantitative relation between pore size and the apparent zeta potential known for pit membranes, the true zeta potential might be calculated for those woods whose pore sizes have been computed by other methods, and, conversely, were the true potential known, the apparent zeta potential could be used to calculate pore size. Lens (29) has made a step in the direction of relating apparent to actual zeta potential in his mathematical treatment of the thickness of the double layer in a slit between two parallel plates. If the pit membrane could be isolated mechanically, its true zeta potential might be measured directly by electrophoresis.

Table 1. Summary of Zeta Potentials on Various Wood Samples

(Double distilled water used except where noted. All measurements on transverse sections 1 cm. thick. Pressure: 20 lb. per sq. in.)

Run No.	Wood	After 20 min.	After 4 hr.	Final	Final time
		mv.	mv.	mv.	Hr.
	SOFTWOODS				
	Non-resinous				
11	Northern white cedar sapwood	1.16	1.29	1.10	17.3
12	Northern white cedar sapwood	....	....	1.58	4.7
13*	Northern white cedar sapwood	1.15	0.88	0.64	14.0
8	Northern white cedar heartwood	2.6	....	1.60	24.0
14†	Eastern hemlock sapwood	1.39	0.62	0.61	6.8
15	Eastern hemlock sapwood	1.21	....	0.96	4.9
16*	Eastern hemlock sapwood	1.30	....	0.33	3.0
17	Eastern hemlock sapwood	1.97	....	....	....
18	Eastern hemlock sapwood	1.50	....	....	....
	Resinous				
20*	Jack pine sapwood	6.08	1.9	1.35	5.3
21*	Loblolly pine sapwood	4.2	....	....	....
22†	Tamarack sapwood	3.3	1.4	1.1	13.4
23	Norway pine sapwood	....	....	0.5	3.5
	HARDWOODS				
24*	White oak sapwood	2.5	1.96	1.82	5.0
25*	Paper birch sapwood	5.3 (5 cm. Hg.)	....	....	....
9	Paper birch heartwood	1.3	....	0.95	12.6

* Single distilled water. † Cell constant approximated.

From the equation for electroosmosis it was seen that if the zeta potential increased, back electroosmosis in the reverse direction would increase. However, if the zeta potential merely remained constant, back electroosmosis might still increase, providing the conductivity were to decrease so that a larger streaming potential could be set up. The latter actually occurs with wood—progressive leaching of electrolytes out of the cell wall frequently resulting in increasing streaming potential during the first half hour, and even for as long as three hours (run 23). However, on further penetration streaming potential and rate of flow both decreased.

Experimental Results and Electrokinetic Theory of Decreasing Flow

The potentials as calculated here are adequate for the chief purpose of these experiments—to discover whether zeta increased with time. Both theory and experiments of other workers (60) have shown that zeta and rate of flow should be inversely related where the rate of flow is changing for electrokinetic reasons alone. In the present work with all species, except one, the apparent zeta potential decreased considerably with decreasing flow. This change is in the opposite direction to that required for an electrokinetic explanation of decreasing flow. The change in potential appears to be a result rather than a cause of the decreasing flow; the factor which causes the flow to decrease also makes the potential change in the same direction. Thus it can be stated that electrokinetic effects are definitely not the primary cause of the falling off of flow, either through wood or through cellulose diaphragms. It is probable that electrokinetic effects associated with leaching do produce a slight decrease in rate of flow as will be discussed under the next heading.

Electrolytes and Rate of Flow

Although electrokinetic effects are thus shown to play no prominent part in producing a decrease in flow, their importance as direct factors in determining the rate of flow through fine capillaries is rapidly becoming realized. Some measurements made in the present work may be of interest in this connection although they were made with a different end in view. In measuring the cell constant for use in the calculation of zeta potentials, 0.1 N KCl (relative viscosity 1.000 at 30° C.) was streamed up through the wood. In table 2 the rate after about

Table 2. Comparison of Rates of Flow of Water and 0.1 N KCl Solution Through Various Diaphragms

Run No.	Diaphragm material	Final rate with water per minute	Rate with 0.1 N KCl per minute	Comparison of KCl rate to rate of water
		cc.	cc.	Per cent
(Pressure: 20 lbs. per sq. in.)				
15	Eastern hemlock sapwood	0.442	1.90	430
5	Cellulose	0.183	0.533	291
......*	Balsam fir heartwood	....	....	282
4	Cellulose	0.251	0.696	277
24†	Paper birch sapwood	13.6	27.0	198
3‡	Cellulose	2.14	3.24	151
C-6 (No. 1)‡	Microporous rubber	0.612	0.904	148
21	Loblolly pine sapwood	2.54	3.5	138
C-6 (No. 2)‡	Microporous rubber	0.598	0.620	104

* Data of Buckman, Schmitz, and Gortner.
† 5 cm. of mercury pressure.
‡ Corrected to 20 lbs. per sq. in. pressure.

300 cc. of KCl had passed is compared with the previous rate with water at the same pressure. All the runs are recorded in which the rate was measured when water was followed by KCl in the same direction.

Two suggested explanations are: (1) a peptizing action of the salt solution on particles supposedly trapped within the pores; and (2) an increased effective capillary size as a result of the decreased thickness of the double layer in solutions of electrolytes. The peptization theory does not fit in with the fact that Buckman, Schmitz, and Gortner (7) found the final rate with water to be regained when KCl was washed out of balsam fir heartwood. Yet in the runs in which the pore size was large this theory serves better, for a change in thickness of the double layer or an increase in back electroosmosis could hardly account for the increase in run 24.[4] In this run probably some of the perforation plates had been ruptured by previous penetration of the wood at 20 pounds per square inch, thus accounting for the high final rate of water at the lower pressure. In run C-6 two parts of the same sheet of microporous rubber of average pore size, 0.2 μ, were penetrated at the same time.[4] Sample number 2 was supported by a copper screen, number 1 was allowed to bulge under pressure.

Because of the bulging of sample number 1 and the fact that many pores were obstructed by the screen of number 2, the initial

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[4] For complete data the reader is referred to the Ph.D. thesis by Bror E. Anderson, on file in the library of the University of Minnesota, entitled "Factors affecting the decreasing rate of flow of liquids through wood, with special reference to electrokinetic phenomena," from which this bulletin is condensed.

rate of flow of number 1 was 2.4 times that of number 2. The final rates were nearly the same, but KCl increased markedly only that of number 1.

According to the electrokinetic theory of the increased rate, the small-pored diaphragms should give relatively greater increases in rate. Thus the non-resinous woods stand at the top of table 2, and the tighter the cellulose is packed (as judged by rate of flow), the greater the percentage increase. It must be noted here that although all the values of table 2 are for the same exterior surface area of diaphragm per centimeter of thickness, the rates of flow for different materials are not relative measures of pore size because their effective areas and capillary lengths differ widely.

Where the increased rate with KCl is due entirely to electrokinetic effects, it should be possible either from theoretical considerations or by first working with rigid materials with fine pores of known dimensions to devise a method for estimating the diameters of pores of ultramicroscopic size from the increase in rate with increasing concentration of electrolytes. The application of this method to the determination of pore sizes in wood would be complicated by the rapid decrease in rate of flow of KCl through wood. The use of a solution isotonic with wood might obviate this difficulty.

If water which had been used in one run were re-used in the penetration of another wood section of the same species, the flow appeared to fall off at about the usual rate. However, when water which had gone through a wood at the start of penetration was used over again toward the end of a run, there was always an immediate slight increase in rate (runs 15, 22, B-5, and B-17)[5] although the water when re-used was at the same or a slightly lower temperature. This effect, which was not noticed when a salt solution was re-used, may have been due to small amounts of electrolytes which were leached from the wood during the first part of the run and so were contained in the water which was re-used. If this is the reason, it would appear that electrokinetic factors actually do account for a small part of the decrease in flow during the first part of a run. But since the rate with KCl does not approach the original rate for water it is evident that changing thickness of the double layer is at the most a minor factor causing decreasing flow. The increased rates with KCl and with HCl serve to show that the thickness of the double layer is appreciable compared with the width of the membrane openings.

[5] See footnote 4 on page 28.

Because of leaching, the double layer would tend to increase somewhat in thickness as penetration proceeded if the size of the pit openings remained constant. However, in the latter part of this work it is suggested that the pit openings actually decrease in size, and in so doing decrease the thickness of the double layer much more than the effect of leaching tends to increase it.

A direct measurement of this effect of electrolytes in the wood on the rate of flow could be made by measuring the permeability of a wood before and after removal of electrolytes by electrodialysis. Electrodialized wood in many respects would be much more suitable for streaming potential measurements. Because of the lower conductivity of electrodialized wood, larger streaming potentials would be built up. The rapid change in conductivity at the start of a run would be reduced, allowing potentials to be measured closer to the start of penetration. The electrolytes present in wood also may directly influence the zeta potential to a slight extent since salt concentrations as low as 0.0001 N have been shown to have an appreciable effect on the potential of cellulose (6).

Explanation of Decreasing Potentials

The next problem is to account for the decreasing zeta potentials which generally occur during penetration. It was shown by Briggs (5) that the zeta potential is independent of rate of flow through cellulose diaphragms of different degrees of packing. The same conclusion might be drawn from the data for four of the five electrokinetic runs which we made on cellulose. In one run the initial zeta potential was about 50 per cent higher than in the other runs, but it decreased rapidly. In the other four runs the zeta potential decreased only slowly.

In studying cellulose and quartz, Bull (8) found that the values for zeta obtained by the streaming potential method were lower than those measured by other procedures. He states, "It may be that the small values for streaming potential with cellulose are due to diminished pore size in the diaphragm packed tightly with cellulose."

The best explanation of the decreasing potentials, for both cellulose and wood diaphragms, is based on the supposition that part or all of the effective capillaries in these diaphragms have minimum dimensions which are below the critical values (see page 12). The double layer is therefore unable to develop to its fullest extent; hence its thickness is reduced and the streaming potential set up is less. The zeta potential calculated from the streaming potential is therefore an apparent rather than an actual value, for it is dependent on the size of the capillaries. As the size of the openings of the pit perforations decreases (for reasons which will be discussed in Part II), the double layer is further repressed (electrical charges on one side of a pore are repelled toward the pore wall by charges of like sign on the opposite side of the pore), and the apparent zeta potential is further reduced. Briggs observed that the zeta potential of cellulose seemed to decrease in proportion to the degree of beating. It is possible, however, that pulps which had been beaten longer had more pores below the critical radius because of their greater fibrillation.

For flow through resinous woods, plotting apparent zeta potential against rate of flow results in straight lines over a wide range (Fig. 2. Note: Figures 2-9 are found on pages 39, 41, 42, 47-50). With these woods, and also with cellulose diaphragms, the rate-potential lines appear to converge toward a point between 1 and 2 millivolts on the potential axis. However, with cellulose the lines are somewhat curved, being shaped similarly to the curves in the rate-potential graph for non-resinous woods.

Consideration of the data on the rate-potential relation for cellulose and resinous woods reveals that as pores decrease in size, thickness of the double layer (as indicated by the apparent zeta potential) decreases at a faster rate. This may be due to the fact that the electrical forces between ions of like charge on opposite sides of a pore vary inversely as the square of the distance.

From theoretical considerations one might expect that the cell constant as measured by the conductivity of the wood diaphragm when penetrated by 0.1 N KCl solution at the end of the run might be in error when used in the calculation of initial zeta potentials from streaming potential measurements. The decrease in effective pore size with penetration would be expected to decrease the conductivity of the continuous columns of KCl solution in the wood. Hence initial zeta potentials calculated from cell constants determined at the end of a run would be too high and would thus account for part of the decrease in apparent zeta potential. There is an indication of some change in this direction in one run in which the cell constant was measured twice during the run. But comparison of resistances with KCl solution measured at the end of short runs with those measured at the end of long runs on eastern hemlock revealed that the resistances were somewhat higher for the shorter runs. This may have been due to adsorption of KCl by the cell wall; more KCl would be adsorbed when the same quantity of KCl solution was passed through a section at the end of a long period of penetration with water than at the end of a shorter period. The reason for this is that at the lower rate of flow following the longer period the KCl solution would be in the wood for a longer time prior to measurement of the resistance. Surprisingly, the electrical resistance of a cellulose diaphragm formed from a suspension of cellulose in KCl solution was found to decrease with time of penetration of KCl solution.

Run 19, in which a section of eastern hemlock sapwood which had been evacuated under KCl solution was used, was made for the purpose of following the changes in the electrical resistance of wood when penetrated by KCl solution. During the first half hour, when changes in effective pore size were the greatest, the variation in electrical conductivity was less than 2 per cent. It therefore appears that the use of the final resistance with KCl for the calculation of the initial zeta potential does not involve too great an error, and the decreasing potentials observed are not due to a change in the cell constant.

An alternative explanation of decreasing potentials with woods is that the nature of the resisting surfaces is changing. This is probably the reason with hardwoods, in which the minimum pore dimensions are above the critical value. If we make the assumption that the vessel walls have a higher zeta potential than either the bars of the scalariform perforation plates or the tyloses, these decreasing potentials will be explained, for rate of flow falls off when these latter structures arrange themselves so as to offer increased resistance to flow.

If the foregoing assumption is true, it would be expected that, since at higher pressures the flow resistance at the perforation plates is decreased (as will be shown in Part II), higher pressures would result in greater zeta potentials through hardwoods. This was found to be true for the one species (paper birch) which was run at two pressures. For white oak there is direct evidence that the structures differ chemically, the outer layer of the tyloses being composed of lignin while the inner walls of vessels are made up of cellulose (21).

It should be noted also that all the softwoods used were of the type through which rate of flow increases faster than the pressure. Since this must be due to an increase in pore size, and since the calculated zeta potential is dependent on pore size below the critical, it is obvious that the apparent zeta potential recorded was dependent upon the pressure used.

The rapid rates of flow through some of the resinous woods used suggest that part of the flow was through the resin canals. Not true structural parts of the wood, the resin canals are merely intercellular spaces surrounded by epithelial cells. The canals themselves are far above the critical radius, but their minimum dimensions are found where they are partially blocked by resin. The potential of the canals would be determined by this resin; at the start the primary walls of the epithelial cells might also be a factor. The decrease in flow through resin canals may be explained by a loosening of fragments of resin, which accumulate at other resin deposits that adhere more firmly. The radius at the constrictions may be below the critical value, at least by the time the first potentials can be measured. With resinous woods, therefore, there will also be a change in the nature of the resisting surface for as penetration proceeds a larger proportion of the liquid must flow by way of the pit membranes. The decrease in potential, however, is probably accounted for better by the decrease in size of the pores used rather than by change to resisting surfaces having lower contact potentials.

Effect of Reversal of Direction of Flow

Both with softwoods and hardwoods, after the rate had decreased to low values in one direction, reversal of direction of flow would often increase the rate by many times, so that in some instances the rate again approached the original rate and even exceeded it occasionally. The rates of flow after the first reversal of direction exhibited a much greater variation in magnitude than did the initial rates of flow for different samples of the same species. With the second batch of seasoned wood (lot No. 2, which was used in Part II) the increased rate on first reversal was not so great. With the few samples of green wood on which reversals were made the effect was not definitely shown. After the first reversal the rate again decreased in much the usual manner. Subsequent reversal after the rate had decreased in the second direction produced comparatively less change in the rate of flow (Fig. 7).

This phenomenon is obviously not the action of pit aspiration (see page 51). It appears that for softwoods different pits or at least different pit perforations are used in each direction in samples on which reversal brings the rate back almost to the original value. Conductivity measurements established that the same cell lumens were used when the direction was reversed, for a second period of rapid leaching was not observed.

A mechanism which immediately presents itself as a likely explanation of this phenomenon in softwoods is that some of the pits were blocked by air on one side of the pit membrane. Some other explanation would then have to be given for flow through hardwoods in which the same phenomenon was observed (Fig. 7-1R). Small amounts of air conceivably trapped beneath the wood section were not a factor since whether flow was up or down through the wood made little difference. Objection to any explanation involving blocking by air in the wood is provided by the fact that unsoaked sections have been shown to have about the same initial permeability as sections soaked by intermittent evacuation under the liquid. Also, soaked sections treated with superheated steam for more complete removal of air likewise exhibited some increases in rate upon reversal of direction.

Other Observations

The non-resinous woods had lower initial potentials and gave much less decrease in potentials. In the two runs of double distilled water through northern white cedar sapwood there was only a slight decrease in potential although flow decreased as usual. Decreases in rate of flow through northern white cedar are, however, of much smaller magnitude than those through hemlock and balsam fir. Single distilled water gave decreasing potentials through northern white cedar (Fig. 6); also in other runs (see table 1 and figure 3) there is some evidence that single distilled water gives lower final potentials. There is little relation between rate of flow through different samples of the same wood and apparent zeta potential. This may be because the rate of flow is dependent both on the size and number of capillaries, while apparent zeta potential is dependent only on the size of the capillaries. In any one sample, however, (Figs. 2 and 3) apparent zeta potential decreases as the rate of flow falls off.

The electrical conductivity of a wood diaphragm always decreased greatly with time of penetration and increased somewhat when the wood was allowed to stand with no flow.

Comparison with Stamm's Results

The potentials reported in table 1 for non-resinous woods do not agree with the values which were assumed by Stamm in his calculation of the size of pit pores from electroosmotic data. Stamm's calculations involved two assumptions: (a) the zeta potential of the pit membrane is the same as the average for wood substance as a whole; and (b) in the small capillaries of pit membranes the same quantitative relations for zeta potential hold as for large capillaries. In the case of streaming potentials it has been definitely shown by several workers (8, 9, 10, and 11) that the same quantitative relations do not hold for small pores, and the criterion of a critical radius below which the ordinary streaming potential equation is invalid was introduced. Although the general statement has been made (12) that in small capillaries electrokinetic measurements lose their validity, experimental data or theoretical calculations as to what should be considered the critical radius for electroosmosis are lacking. Streaming potential is not the exact counterpart of electroosmosis. The velocity gradients from the wall to the center of a pore for the latter phenomenon differ considerably from the ordinary parabolic diagram for viscous flow (39). In electroosmosis the point representing the average velocity is closer to the wall of the capillary. In view of this fact, it would not be surprising if the effect of very small pores were different for the two cases, so that assumption (b) might possibly be valid for the one case and not the other.

The electrokinetics of the pit membrane might be compared with those of cellophane, in which the pores are smaller, hence the effect of repression of the double layer should be more marked. Through cellophane, electroosmosis is a very significant and measurable quantity, whereas streaming potential is not. From the data of other workers who attempted, unsuccessfully, to show the equivalence of the electroosmotic and streaming methods with various fine-pored diaphragms, there seems to be no reason for expecting the two methods to yield identical results when distilled water is used with softwoods.

It should be emphasized here that there is no *a priori* reason for expecting the potential of pit membranes to be the same as that of wood as a whole. Since between its cellulosic primary walls the pit membrane possibly contains ligneous intercellular substance, a knowledge of the potential of lignin is also desirable. From Lottermoser's flocculation experiments (30) it appears likely that lignin has a more strongly negative zeta potential than cellulose. This was confirmed in streaming potential measurements through two different lignin preparations (runs 27, $\zeta =$ 18 mv.; and 29, $\zeta =$ 19 mv.). Lignin as it exists in wood may, however, have a different potential. If lignin is the important constituent of the surface of the pit membrane perforations, the true zeta potential of pit membranes probably is somewhat more negative than −13.6 millivolts.

SUMMARY OF RESULTS OF PART I

The observed change in zeta potential with decreasing rate of flow (constant pressure) is in the opposite direction to that required for an electrokinetic explanation of the decreased flow. The decrease in potential appears to be a result rather than a cause of decreasing flow and, at least in the case of softwoods, to arise from a decreasing effective pore size. Our studies definitely indicate that the falling off of flow either through wood or through cellulose diaphragms is not primarily caused by electrokinetic effects.

When distilled water is followed by 0.1 N KCl solution, rate of flow may be increased by many times. Proportionately greater increases are obtained with the diaphragms having the smaller capillary sizes. This fact has suggested the possibility that the percentage increase in rate with salt solutions could be used to estimate pore size.

The apparent zeta potential found for the pit membranes by the streaming method does not agree with that assumed by Stamm. His electroosmotic method of estimating pore size was based on hazardous assumptions, but the fair agreement in the results by different methods indicates that either the assumptions were not far from correct or else they involved compensating errors.

Variable increases in rate of flow upon first reversal of the direction have been frequently observed. Electrical conductivity measurements during flow have shown that, in all probability, the same cell lumens were used before and after the direction of flow was reversed. Pit aspiration does not appear to be a factor in volume changes upon direction of flow reversal.

PART II

FURTHER STUDIES ON THE MECHANISM INVOLVED

INTRODUCTION

Part II is a heterogeneous collection of experiments on penetration of woods and other permeable materials. The purpose of these runs was to collect data under different conditions, generally allowing only one factor to vary at a time, in order that several of the phenomena observed in wood penetration might be better understood. Since in Part I the electrokinetic explanation was found inadequate, it seemed advisable to check the two other explanations of decreasing flow frequently resorted to in the literature: swelling and pit aspiration. Several other possibilities which occurred to the writers are also investigated in this section.

In Part II the effect of change of direction of flow through wood was more extensively studied. Runs were made also on other porous materials so that the effects of various variables might be compared with similar data for wood. In several of these materials the structure is simpler and pores are microscopic rather than ultramicroscopic—hence fewer possible mechanisms for producing decreasing flow suggest themselves.

APPARATUS AND METHODS

During the experiments of Part I preliminary observations on the effect of a series of rapid reversals of direction of flow had indicated that this procedure often produced a very marked effect on the rate of flow. For many of the runs of Part II it was considered advisable, therefore, to modify the apparatus used in Part I so that this operation could be more readily and accurately performed. For several of these runs other modifications of the apparatus of Part I were used. Those more frequently employed are described as follows:

Apparatus I was the same apparatus as was used in Part I. Unless otherwise stated, all runs with this apparatus were made at 30° C.

Apparatus II (Fig. 1) had as its distinctive feature a provision for rapid alternation of direction of flow. A three-way stopcock (A) on the supply side was attached to a similar stopcock on the exit side by embedding the stopcock handles in corks and centering the corks, one on each side of a 5-inch cork. A belt running along a groove in the latter was turned by a small wheel on the shaft of the worm gear of an oscillating electric fan (B). In one hour this device provided about 200 alternations of direction of flow (100 complete stopcock rotations), allowing a few seconds flow with each alternation. For holding the samples, three pairs of rubber stoppers, each with a beveled hole 1.7 cm. in diameter, were fixed between two iron plates (C). The samples could be clamped between these pairs of stoppers either as wood plugs of 1.7 cm. diameter encased in glass cylinders as in Part I or, more conveniently, as 1½ inch x 1½ inch sections as shown in the figure, as penetration in other than the longitudinal direction was generally negligible.

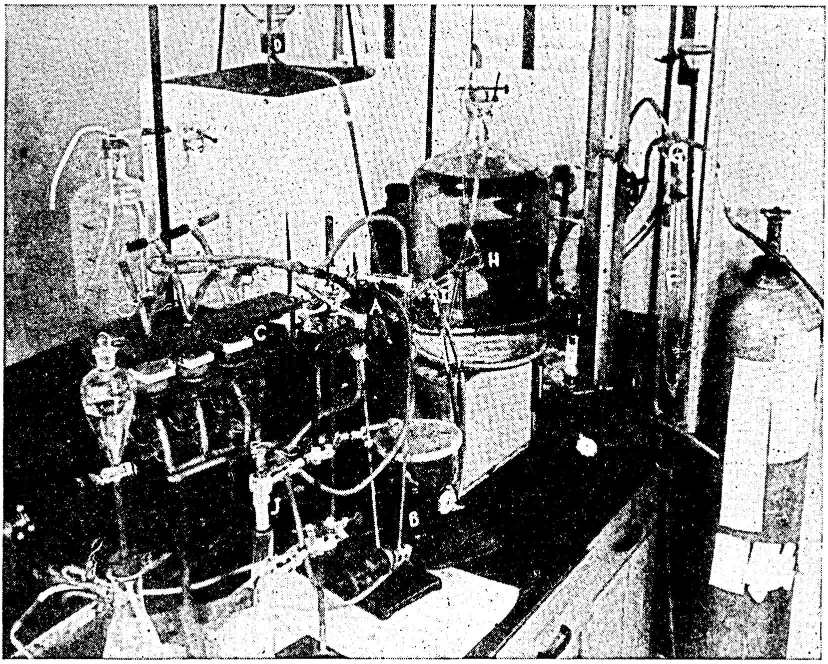

Fig. 1. Apparatus II Used in Trial Runs

In several runs with Apparatus II where a relatively low pressure was required only the head of the liquid was utilized by lowering the exit tube the proper distance below the level of the liquid in the supply bottle. For long runs a jug inverted over a reservoir (D) was used, while in runs using de-aired liquids, two one-gallon bottles in series (E) were generally employed. The apparatus (C) could be readily inverted to remove air trapped below the wood, and the sample could be run in this position if desired. The Y tube connections made it possible to measure the rate of flow through any one of the samples without interrupting flow through the other two. A single pair of Mohr pipettes (F) (as in Part I, with the exit T tube [G] adjustable to the level of the liquid in the supply bottle [E]) was used for measuring the rates through each of the samples in turn. By proper arrangement of pinch-clamps, three samples clamped in this apparatus could also have been run in series, but most of the runs in series were made in the earlier apparatus. A thermometer (I) was inserted in the line before the liquid entered the wood.

Apparatus III resembled the apparatus used by Erickson, Schmitz, and Gortner (13) for salt solutions, except that it provided for change in direction of flow. It was the forerunner of Apparatus II, which it resembled except for lack of stopcocks, a different method of measuring flow, and the fact that the rate of flow could not be measured while the apparatus was inverted.

Apparatus IV consisted simply of two ground glass flanges, or two rubber stoppers with matched holes of a given size, between which the porous material was clamped. One glass flange or rubber stopper was connected with a liquid supply using a minimum of rubber tubing.

An even simpler apparatus was that used for running dowels (Fig. 1, J). A piece of large rubber tubing was fitted over one end of the dowel and attached to a supply of liquid. Some of the dowels were evacuated dry and the liquid then run up through the wood to further displace the air (Fig. 1, K). This method did not appear to have any advantages, however, for when these dowels were subsequently evacuated under the liquid much more air bubbled out.

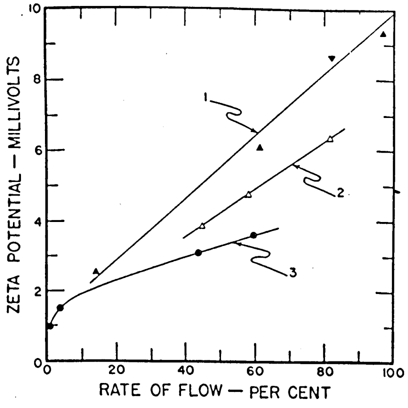

FIG. 2. RELATIONSHIP BETWEEN APPARENT ZETA POTENTIAL (IN MILLIVOLTS) AND RATE OF FLOW (IN PER CENT OF THE MAXIMUM RATE) OF DISTILLED WATER THROUGH RESINOUS SOFTWOOD SAPWOODS*

1. Run 20—Jack pine
2. Run 21—Loblolly pine
3. Run 22—Tamarack

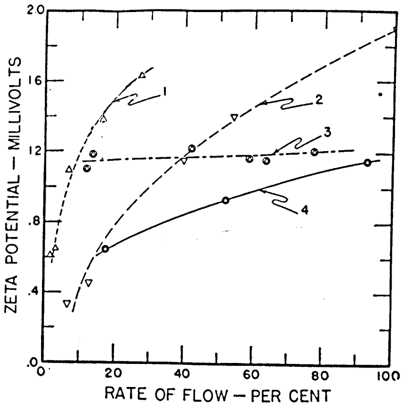

FIG. 3. RELATIONSHIP BETWEEN APPARENT ZETA POTENTIAL (IN MILLIVOLTS) AND RATE OF FLOW (IN PER CENT OF THE MAXIMUM RATE) OF WATER THROUGH NON-RESINOUS SOFTWOOD SAPWOODS*

1. Run 14—Double distilled water through eastern hemlock
2. Run 16—Single distilled water through eastern hemlock
3. Run 11—Double distilled water through northern white cedar
4. Run 12—Single distilled water through northern white cedar

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* All runs with wood are for sections 1 cm. thick and pressures of 20 pounds per square inch (103.8 cm. Hg.) unless otherwise stated. Triangles with vertex up indicate that flow was up through the wood in direction A. Triangles with vertex down indicate that flow was down through the wood in direction B.

DISCUSSION OF RESULTS

To treat concisely the data which were collected for the purpose of investigating other possible explanations of the decreasing rate of flow, the results of Part II will be discussed under three headings: (A) Various other theories on decreasing flow in relation to observed data. (B) The nonlinear rate-pressure relation. (C) Proposed explanation of decreasing flow.

A. Theories on Decreasing Flow

1. Swelling.—It is conceivable that certain parts of a woody structure might not be wet by the usual procedure of intermittent evacuation under a liquid. For instance, the last portions of air which cannot be removed from the wood by evacuation might remain lodged in the pits, preventing their membranes, which are the structures determining the rate of flow, from being wetted. Or the composition of the pit membrane might be such that it is not easily wet by water even when no air is present. Then the water would exhibit a convex miniscus at the entrance to a pit perforation.

Were swelling a factor, it would be expected that once penetration was started, further swelling, if it did occur, would continue for a time after penetration ceased so that when flow was resumed the rate would have decreased still more. This was not found to be the case, rates of flow through softwoods being more frequently increased by standing. Also, alternations and spurts in one direction would be expected to cause decreases rather than the increases which do result.

2. Plugging by Particles.—The use of an apparatus in which the direction of flow through the wood could be reversed brought out several characteristics of flow which at first were interpreted as evidence of a plugging by particles. For instance, upon reversal of direction (except in those instances where first reversals caused rate of flow to return approximately to the original) the rate generally increased for a few minutes to half an hour before resuming its decrease. This would be anticipated if reversal caused particles to be washed out of the pit perforations.

This phenomenon, however, is perhaps better interpreted as a time lag required for each membrane to come to equilibrium with the pressure gradient running in the opposite direction across it. With any material capable of giving decreasing flow being penetrated at a low pressure, when flow was permitted at a higher pressure for a time, after which the pressure was returned to the original, it was found that the rate of flow had been considerably increased. The rate would then decrease over a period of minutes or hours (depending upon the material) even on standing with no flow. Clearly these materials required considerable time to return to equilibrium at the lower pressures. One might then expect that in going to a higher pressure a time lag would also be involved. This was demonstrated by the increasing rates of flow occasionally noted during the first few minutes after pressure was applied; it has also been reported by other workers. More often, however, the great decreases in rate masked this effect.

The fact that the time lag is almost always present is brought out when the data are plotted on log-log paper. Figures 4 and

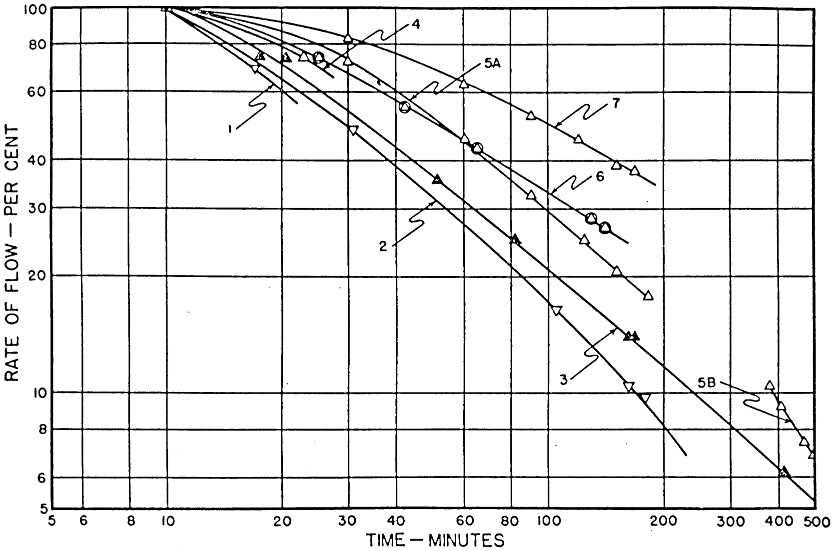

FIG. 4. RELATIONSHIP BETWEEN TIME AND RATE OF FLOW (IN PER CENT OF RATE AT 10 MINUTES) OF DISTILLED WATER THROUGH NON-RESINOUS SOFTWOOD SAPWOODS*

1. Run 18—Double distilled water through eastern hemlock
2. Run 16—Single distilled water through eastern hemlock
3. Run 14—Double distilled water through eastern hemlock
4. Run 17—Double distilled water through eastern hemlock

5A. Run D-28—Unseasoned, unevacuated balsam fir section 5 mm. thick run at 5 cm. of Hg.

5B. Continuation of same run after washing out attempt

6. Run D-9—Unseasoned eastern hemlock section 5.38 mm. thick run at 5 cm. Hg.
7. Data of Erickson, Schmitz, and Gortner (17) for seasoned eastern hemlock at 5 cm. Hg.

* See footnote for figures 2 and 3.

5 show that when the data are plotted in this manner, a straight line function results after the first 10 to 60 minutes of flow. Below 10 minutes a curved function resulted for all the runs of these graphs (except Curve 1, figure 5, on an alundum disk containing trapped particles), indicating that the rate decreased at a proportionately slower rate during the first several minutes. A large number of the runs were graphed in a similar manner, only a few of these curves being reproduced in this bulletin. With almost all softwoods and other diaphragms giving decreasing rates of flow (except hardwoods) the same types of curves were produced, with a nearly linear relation resulting after the preliminary period. The log-log plot then produced a straight line until the run was discontinued (17 hours for runs 11 and 12 on northern white cedar; 34 hours for run A-1 on loosely packed cellulose). With most of the plots there was a very slight downward curvature even after several hours, indicating that the rate tends to decrease slightly faster than would be calculated from an equation which assumes a perfect log-log function.

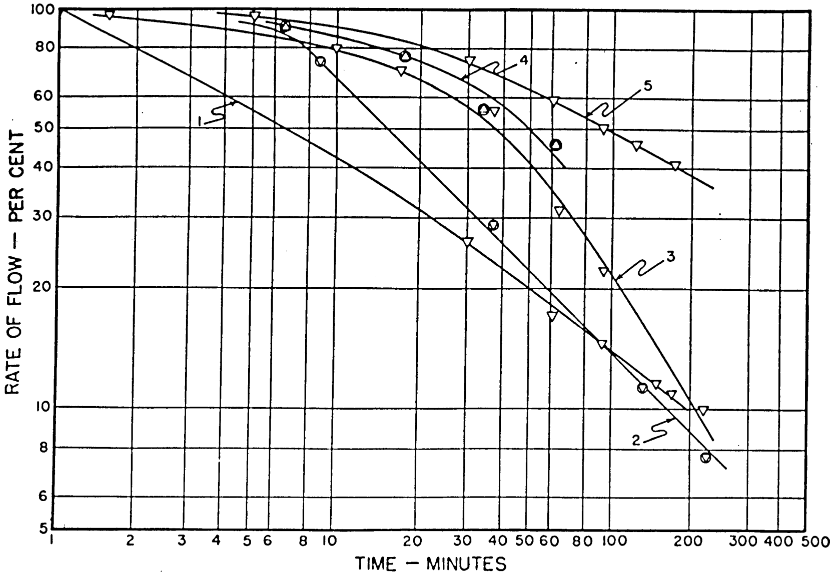

FIG. 5. RELATIONSHIP BETWEEN TIME AND RATE OF FLOW (IN PER CENT OF THE RATE AT ONE MINUTE) OF DISTILLED WATER THROUGH POROUS MATERIALS*

1. Run C-15—Alundum disk at 5 cm. Hg. pressure
2. Run 9—Paper birch heartwood
3. Run C-14—Cotton cloth at 1 cm. Hg.
4. Run C-16—Carbon disk at 100 cm. Hg.
5. Run C-11—Two sheets of punched cellophane at 5 cm. Hg.

* See footnote for figures 2 and 3.

All of this suggests that no equilibrium rate exists for flow through pit membranes. Erickson, Schmitz, and Gortner (13) believed that flow had practically reached an equilibrium rate at the end of 2.75 hours. When plotted logarithmically, however, their data, from which Curve 7, figure 4, is drawn, do not indicate that any equilibrium is reached with softwoods. The designation of any particular time as the point at which the equilibrium rate has been reached is therefore more or less arbitrary when flow is through pit membranes. With paper birch, a hardwood, some of the data indicate that an equilibrium is actually approached.

The increasing rate following reversal of direction, consequently, is probably not caused by a washing out of particles but rather by a slow enlargement of the pores of the membrane by flow in the reverse direction. A simple explanation would be that on flow reversal the membrane bulges slowly in the other direction. A better explanation will be put forward later.

A second effect which is characteristic of plugging by particles is the increased rate of flow following successive rapid alternations of direction of flow. This occurred with most woods studied, with several samples the rate being increased by 50 or 100 per cent by this process (runs D-2, 7, 9, 11).[6] With various cellulosic materials alternations of direction of flow also produced increased rates of flow. The greatest effect of alternation of direction of flow was found in experiments on a diaphragm containing trapped particles (run C-16) in which the increases were of the order of two to six times, and with loblolly pine sapwood (run E-1) where the increase was 1300 per cent. Under the conditions used, alternations during runs at higher pressures (100 cm. Hg.) were more effective than alternations at lower pressures (5 cm. Hg. or less). Alternations of direction were most effective in increasing the rate of flow if the rate had already been decreased to a low value by penetration. In several cases it was even possible to increase the initial rates somewhat. With paper birch it appeared that those samples which had the lower initial rates of flow were those whose initial permeability was increased to the greater extent. In other words, a preliminary treatment by alternation of direction of flow considerably reduced the otherwise large variation in initial rates of flow.

Except when the alternation procedure was used to increase initial rates of flow, the amount of liquid flowing through the wood with each alternation was very small, probably consider-

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[6] See footnote 4 on page 28.

ably less than one milliliter in most instances. The fact that it was the same small volume of water that was passed back and forth through the wood in these treatments probably made no difference, for when pinch-clamps were placed so as to cut one phase of the alternations, resulting in intermittent flow in one direction (referred to as "spurts"), much the same effect was produced, but to a lesser degree. After additional spurts would no longer increase the rate of flow, but gave decreasing rate instead, the alternation procedure would further increase the rate. The action of these procedures was probably one of vigorous agitation of the membranes of wood, with little actual flow. This interpretation is supported by evidence from numerous runs in which a series of measurements of rates of flow in alternate directions were made. During each measurement about 15 mls. traversed the wood. It was generally found that the rate of flow decreased faster by such a process than when penetration was in one direction only for an equal time. (Sections in which the first reversal greatly increased the rate are exceptions, however, as penetration for some time in the second direction—in which the rate was high—increased the previously low rate in the first direction.) With a carbon diaphragm it was found that much of the increase in rate of flow following a period of alternations of direction was rapidly lost either with subsequent penetration or on standing with no flow. In this respect it differed from wood.

In the case of cellulose diaphragms one interpretation of the increase in rate of flow produced by alternations of direction is that the natural or mechanical equilibrium position of the fibers is one which offers a lower resistance to flow. This mechanism will be considered further and applied to wood later in this discussion.

Some evidence for a plugging theory was also found in runs on diaphragms composed of heterogeneously sized granular materials. The pressure exponents were of the same order, and penetration at high pressures increased the rate of flow at low pressures. The plugging theory will be further discussed in the following three sections.

(a) *Particles from the walls of the cell lumen or vessel segments.*—It was possible with certain softwoods to cut sections of such a thickness that over half of the volume of flow was through channels in which only one pit membrane had to be traversed; each tracheid of such a channel would be open at one end. Such a section is referred to in this work as a "one-membrane" section. "Zero-membrane" sections through which flow was largely through open tracheids cut at both ends were also used. Unless otherwise specified, other data refer to poly-membrane sections.

Evidence against a particle plugging theory was derived from studies of one-membrane sections. Unlike an ordinary filter bed, such sections could not be backwashed to increase flow. Penetration in the opposite direction instead generally decreased the rate of flow in the original direction. But when the pores of eastern hemlock were plugged by sols having particles of small enough size so that many passed through in the filtrate, backwashing could readily be effected (run D-6). Attempts at washing the postulated particles out of zero-membrane sections on to microporous rubber connected in series with the wood section yielded no evidence of a plugging of the microporous rubber by particles washed out of the cell lumen.

In a run on a one-membrane section of balsam fir sapwood flow was successively decreased by flow of a few milliliters in alternate directions, and increased by a total of 590 alternations. Subsequent flow in the previous direction showed that the rate then decreased slightly more rapidly than before. (Compare the slopes of Curves 5A and 5B of figure 4.) Thus there was no evidence of a washing out of particles.

With a hardwood, paper birch sapwood, evidence of a washing-out action was also lacking. Rates of flow at 5 cm. of mercury pressure through two matched samples were, by chance, almost identical during the last 1.5 hours of a 2.7 hour run (at the end of which time the rates had decreased to about 35 per cent of the initial rate), while the initial rates of the two sections had differed by only 7 per cent. By a series of 300 rapid alternations of direction of flow the rate through one of the sections was increased by 45 per cent. The penetration of this section was then continued in the original direction until the rate of flow was again down to that of the control. Simultaneous penetration of the two sections was then resumed; one hour later they still showed no significant differences in rates of flow. One-half gallon more of water was run through. The rate of the "washed" sample was then 8.5 per cent of the rate immediately before the alternations of direction; the rate for the control sample calculated on the same basis was 13.5 per cent. Thus again alternations of direction produced subsequently a slightly more rapid decrease in rate of flow rather than a less rapid decrease as would be expected if particles were washed out.

(b) *Particles trapped within the pit membrane.*—The pit membrane might be regarded merely as a specialized part of the compound middle lamella. As such it might likewise be considered to be made up of the two primary walls of contiguous cells plus the intercellular substance between them. This entrapped substance would give flow phenomena characteristic of particles except that it could not be washed out. Objection to this hypothesis is that one might then expect the initial decreases in rate of flow to be very much more rapid than they actually are for the particles would be contained in a very narrow space between the two walls. Intercellular substance of Douglas fir is known to consist largely of lignin. Since Stamm found that the permeability of Douglas fir sections could be greatly increased by the use of lignin solvents, it would appear that, if we assume the resin canals to be inactive, there must be some lignin in the pit membranes.

(c) *Particles contained in the liquid.*—Numerous workers have shown the necessity of obtaining a distilled water free from particles for use in ultrafiltration. When distilled water was allowed to stand a few days, an increased viscosity as measured by ordinary methods has been reported by several workers. In this work no differences in rate of flow could be detected in flow of distilled water as compared with flow of freshly double-distilled water through wood sections.

After penetration by a solution of mercuric chloride made up from distilled water, dowels of eastern hemlock and balsam fir sapwoods were cut in half. The rate of flow through the half of the section that remained (which contained the end through which the liquid had entered the wood) was increased not quite in proportion to the decrease in length after the necessary corrections were made, giving evidence that there was a slight amount of plugging which could be traced to particles in the liquid. It was apparent, however, that the large part of the decrease in rate of flow had to be attributed to other causes.

3. Effect of air.—(a) *Air in the liquid.*—If air is dissolved in the liquid under pressure so that when the pressure is reduced as the liquid traverses the wood a supersaturated condition results, air may be released into the pores in the wood. It appears that even when water is merely aerated at atmospheric pressure by shaking the reservoir bottle and allowed to stand a while before use, the subsequent rate of flow decreases along a steeper slope because water at the bottom of the bottle is saturated with air under a pressure slightly greater than atmospheric, due to the head of water in the bottle (run B-17). The very slightly supersaturated condition which results when this water traverses the diaphragm seems to be enough to produce a more rapidly decreasing rate of flow.

In the present work care was taken to see that no such supersaturation unknowingly existed.

(b) *Air in the wood.*—Since all the air could not be removed from wood by intermittent evacuation under the liquid, the possibility existed that air was gradually accumulating in the pits and blocking flow. This would offer an explanation for the greatly increased rate of flow often obtained after first reversal of direction of flow, were it not for the fact that when the direction of flow was immediately returned to the original the flow was not found to have been increased very greatly by a backwashing of such air out of the pits (runs 11, D-8b, and D-28). It might, of course, be argued that it would be difficult completely to backwash this air out of the pits because of the overhanging nature of the secondary walls.

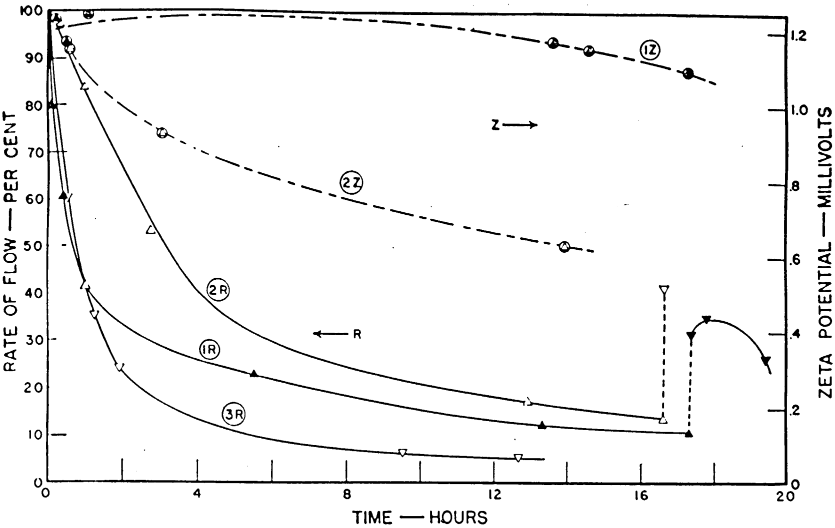

FIG. 6. RATE AND POTENTIAL CURVES FOR VARIOUS SYSTEMS*

1R Rate of flow of double distilled water through northern white cedar sapwood, run 11
1Z Zeta potential for run 11
2R Rate of flow of distilled water through northern white cedar sapwood, run 12
2Z Zeta potential for run 12
3R Rate of flow of distilled water through a loosely held cellulose diaphragm, run A-1

* For R curves use left hand scale; for Z curves use right hand scale. Triangles with vertex up indicate that flow was up through the wood in direction A. Triangles with vertex down indicate that flow was down through the wood in direction B. Pressure was 20 pounds per square inch on sections 1 cm. thick for all runs on woods.

To remove more completely the air from eastern hemlock sapwood which had been evacuated under water, some sections were treated in a closed container with steam superheated to 110° C. The principle involved was that the water in the wood would be vaporized, and in passing out of the wood should sweep most of the residual air out with it. At the end of one-half hour the steam in the container was allowed to condense and draw in water to cover the wood so that the wood had no further contact with air, except for the few seconds required to transfer it to the apparatus.

One of these samples was then reaerated by blowing air through, and re-evacuated under water. This method of obtaining a control sample is open to criticism because probably only the larger capillaries were aerated by this process. The aerated sample gave a lower rate of flow than the matched sample not aerated, but the difference was not significant. These steamed samples still gave decreasing rate of flow although the decrease was not so rapid. The less rapid decrease is better attributed to some specific effect of steaming on the pit membrane rather than to removal of air.

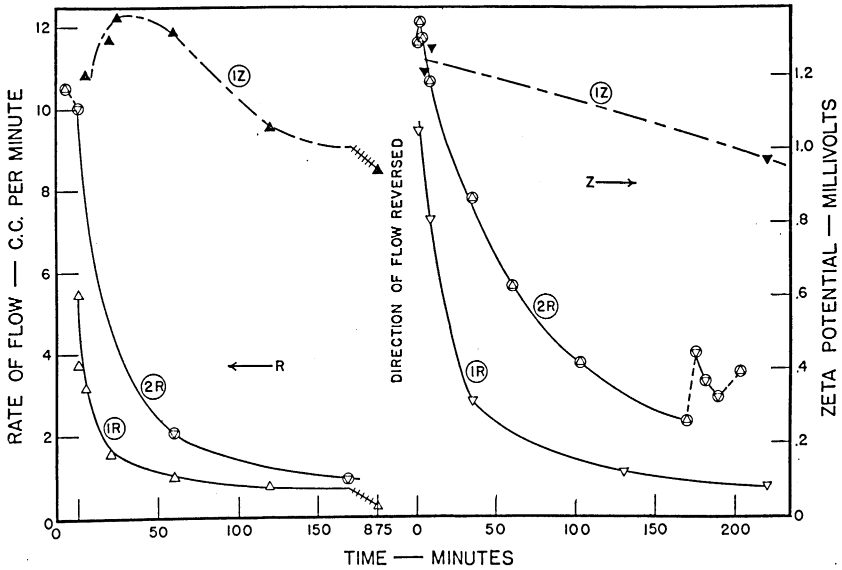

FIG. 7. RATE AND POTENTIAL CURVES FOR VARIOUS SYSTEMS*
1R Rate of flow of double distilled water through paper birch heartwood, run 9
1Z Zeta potential, run 9
2R Rate of flow of distilled water through eastern hemlock sapwood, run D-5
* See footnote for figure 6.

4. Decreasing flow through cellulose.—The similarity in the curves for flow of water through filter paper and cotton cloth with those for wood (Figs. 5, 6, and 8) had suggested that the explanation for the decreasing flow might be the same for all such materials. This possibility of a general explanation for the phenomenon was one of the reasons that the electrokinetic changes during flow were first investigated. It now seemed advisable to consider other mechanisms which might account for the decreasing flow through cellulose diaphragms.

(a) *Packing effect.*—If a diaphragm were compressed by the pressure gradient across it, the average pore size would be reduced, both by the compression of the slits parallel to the surface of the diaphragm (thereby decreasing the pore size in the tortuous path of liquid flow) and by a pressing of more fibers into the void spaces in the path of flow. Although there would also be some shortening of the path of flow, the net effect of compression of a cellulosic filter material should be a decrease in rate of flow.

The objection to attributing the falling off in rate of flow to a compression of the membrane is that even with quite loosely

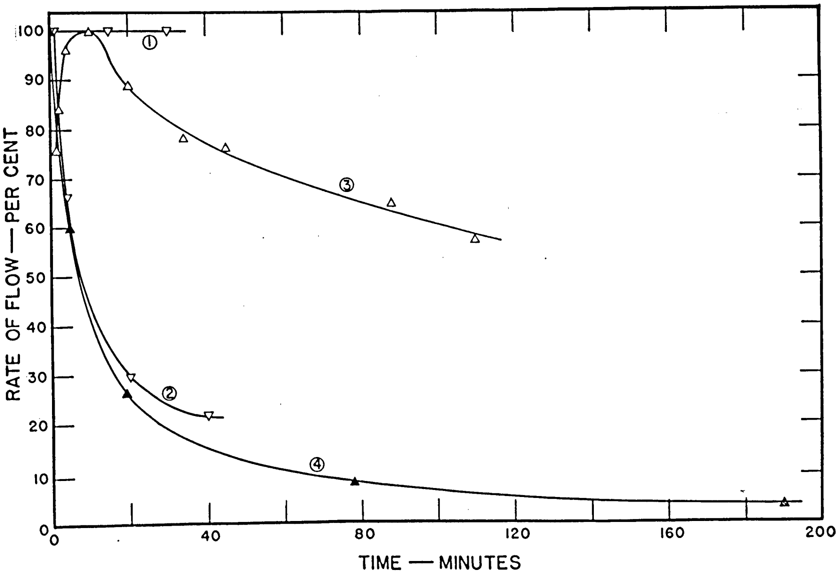

Fig. 8. Rate of Flow Curves for Various Systems*

1. Rate of flow of benzol or 95 per cent ethanol through filter paper, run A-8
2. Rate of flow of distilled water through filter paper, run A-8
3. Rate of flow of 95 per cent ethanol through western hemlock heartwood
4. Rate of flow of distilled water through western hemlock sapwood, run D-3

* See footnote for figure 6.

formed cellulose mats, made by pouring a cellulose suspension through a glass tube having a 12-mesh screen at the bottom end, using only a slight vacuum and no tamping, no packing effect on the cellulose mat could be observed at a low pressure which gave rates of flow which fell off rapidly. A theoretical explanation of why such a compression does not take place will be put forward later.

(b) *Unstable condition of the diaphragm.*—In the case of a packed diaphragm or one dried after it was formed (filter paper), certain stresses may exist in the form of a compression of the fibers. The agitation of the flowing liquid could conceivably produce rearrangement of the fibers to reduce these stresses. Such a rearrangement would naturally fill up more of the void spaces and thereby reduce pore size. An unstable condition of this type could conceivably be produced in the pit membranes and scalariform perforation plates when the last free water is removed from the interior of the cells.

According to this hypothesis one would expect that rapid alternations of direction of flow would serve to relieve such

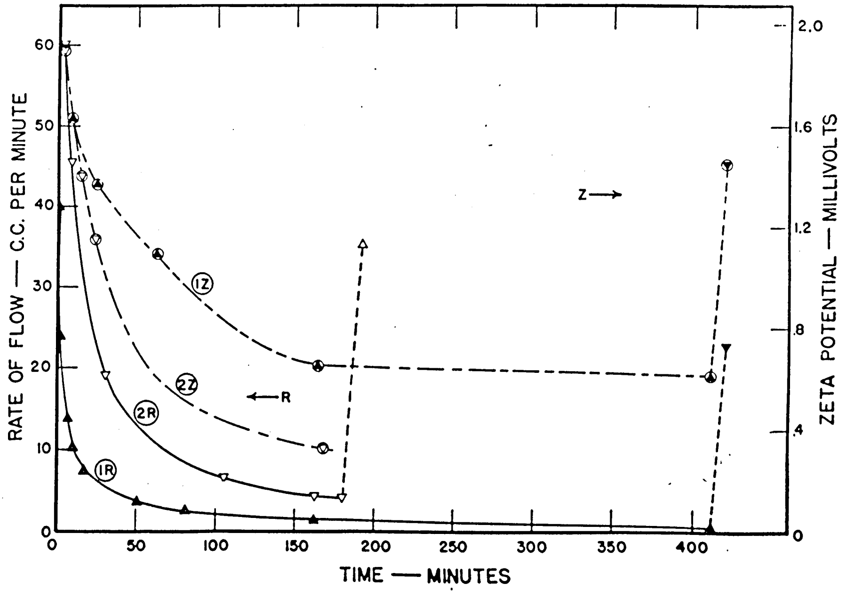

FIG. 9. RATE AND POTENTIAL CURVES FOR VARIOUS SYSTEMS*

1R Rate of flow of double distilled water through eastern hemlock sapwood, run 14
1Z Zeta potential, run 14
2R Rate of flow of distilled water through eastern hemlock sapwood, run 16
2Z Zeta potential, run 16

* See footnote for figure 6.

stresses. The opposite effect, an increase in rate of flow after this treatment, was, however, almost invariably observed.

(c) *Peptization.*—According to this conception, particles of cellulose may be broken off (or peptized) and accumulate at constrictions. This version would not help to explain the initial very rapid decreases through loosely held cellulose. Nor could the comparatively rapid decrease in rate of flow through a well-packed diaphragm formed from cellulose which had been thoroughly washed on a 60-mesh screen be explained on this basis.

5. Valve effects.—(a) *Pit aspiration.*—In pit aspiration the torus is pushed over to contact the overhanging secondary wall, thus blocking off most of the permeable area of the membrane. Such action apparently takes place in formation of heartwood and, with some woods, in seasoning. The argument against pit aspirations taking place during penetration has been based on the rate-pressure relation in woods. It was maintained that pit aspiration should take place more readily at higher pressures; therefore, doubling the pressure should give less than twice the rate of flow. Since the opposite effect is generally observed, the theory has been in disrepute. The argument, although strong, is not conclusive. Doubling the pressure, for example, would give four times the turbulence about the pits, which might retard pit aspiration.

Not previously pointed out as evidence against pit aspiration as a general explanation of decreasing flow are the data of Erickson, Schmitz, and Gortner (14) showing that paper birch and white oak in tangential or radial sections give about the same proportionate decreases in rate as do similar sections of softwoods. This is despite the fact that in the pits of fiber tracheids and fibers the membranes are not capable of movement; hence, since pit aspiration cannot be a factor in hardwoods, it would not seem likely to be the causal factor in softwoods.

In a number of runs on various woods, after the rate had decreased in one direction, flow was allowed in the other direction for a short time; then the rate was again measured in the original direction. The change in rate of flow brought about by this short period of backwashing was not great, and decreases were noted about as often as increases. If pits were aspirated by flow in one direction, one might expect some of them to be opened up again by flow in the opposite direction. This argument, however, is not in itself conclusive because back flow might also aspirate pits in the second direction.

(b) *Valve action at the pit membrane surface.*—When minute holes or slits were punched in a sheet of cellophane "600" and the sheet then penetrated by water from the opposite direction from which the holes were punched, the rate of flow fell off slightly with time. This decrease is readily explained as the result of bulging out of the jagged edges around the perforations. The flowing liquid would tend to force these edges back, thus decreasing pore size. When two such punched sheets (to simulate the two primary walls of the pit membrane) were placed together with their jagged edges outward, the rate of flow decreased about as rapidly as with wood at the same pressure (compare Curve 5, figure 5, with Curve 7, figure 4), and gave a similar linear plot on log-log paper.

With this double membrane diaphragm of cellophane a sharp increase in rate was expected upon first reversal of direction of flow, but instead there was no flow at all when the direction was reversed after penetration in one direction. Another respect in which flow through this double membrane differed from the flow through wood was that when at this point flow was permitted for a few seconds at ten times the pressure previously used and then the pressure was dropped to the original value, the rate was found to have increased beyond the initial rate instead of increasing only moderately. After this increase the rate of flow again fell off and after the rate had decreased below the previous initial rate, the rate of flow curve could be plotted so as practically to coincide with previous curve. Flow in reverse direction this time was 7 per cent of final rate in the original direction.

In general the evidence from these experiments did not point to such a valve action in wood. Other experiments using two sheets of cellophane whose pores had been etched to larger sizes by $ZnCl_2$ solution did not indicate that the two-layer conception of the pit membrane had any particular value although some decreases in rates of flow were observed in these runs.

(c) *Valve action within the pit membrane structure.*—The mechanism which will be proposed in this work might be considered to fall under the above heading. Its discussion, however, will be deferred until later.

B. The Pressure-Rate Relation

The disproportionate increase in rate of flow which is produced when the pressure is increased in the penetration of softwood sections of most species which have been investigated is also found with diaphragms of other materials. Wood and cotton cellulose, and also diaphragms of granular materials or sections of hardwoods when they show decreasing rate of flow, likewise exhibit this disproportionate increase in rate of flow with increasing pressure. In this study the exponents of the pressure which would make the rate increase as a linear function were calculated. The exponents for increasing pressure were found to be greater than the corresponding exponents for decreasing pressures. In other words, flow at a higher pressure results in an increased rate of flow when the pressure is returned to the original lower value. This increased flow is a function of time; the rate will decrease on standing with no flow (see page 40).

With softwoods the phenomenon has been attributed to a bulging of the pit membrane; with filter cloths other unsatisfactory explanations have been proposed (see page 16). The absurdity of picturing the entire phenomenon as a result of an actual bulging of the pit membranes may be shown by calculation. For instance, in run 51 the rates of flow through eastern hemlock sapwood at pressures of 5 and 103.8 cm. of mercury were .072 and 29.1 mls. per minute, respectively. According to the law of Poiseuille (assuming circular pores):

$$\frac{5 \text{ x } 29.1}{103.8 \text{ x } .072} = \left(\frac{r_2}{r_1}\right)^4 \qquad \text{and} \qquad \left(\frac{r_2}{r_1}\right)^2 = 4.4$$

where r_1 and r_2 are the radii of the pores at different pressures and $\left(\frac{r_2}{r_1}\right)^2$ is the ratio of their areas.

Were the effect produced by bulging, the total membrane area would likewise be expected to increase by about 4.4 times—obviously an improbability, since if the membrane were bulged to form a perfect hemisphere the area would only be doubled. This example was not an extreme case, for the pressure exponent was about the average (2.0).

Up to this point we have been attacking the problem largely from a biochemist's point of view; we have considered the flow of fluids through small capillaries as somewhat of a special case in which ordinary conditions of viscous flow were possibly complicated by other factors such as electrokinetic properties and plugging by colloidal material. It will now prove profitable to approach the problem from an engineering angle and study certain aspects of the flow of fluids past obstructions in the path of flow. The discussion will be divided under two headings. Under the first we shall consider the effects which are produced on flow in the primary direction, that is, in the same direction in which the fluid was moving before encountering the obstructions. Under the second we shall consider the effects on flow in the secondary directions, that is, in directions perpendicular to the path of flow of the main body of fluid.

1. Flow in the Primary Direction.—It is known that if two spheres are suspended a short distance apart in a large volume of moving liquid in such a way that their line of centers is perpendicular to the path of flow, these spheres will tend to move toward each other (see Prandtl and Tietjens [37] for illustrations). This apparent attraction between the spheres is explained on the basis of Bernoulli's theorem, which will be taken up in more detail for the similar and more pertinent situation next discussed.

Consider two parallel fibers (of either cylindrical or somewhat rectangular cross section), suspended across the path of a moving fluid with their long axes perpendicular to the direction of flow. The fluid as it approaches each of the fibers divides so that one portion passes between the fibers, while the remainder passes around on the opposite sides of the fibers. The volume of fluid which is deflected into the space between the fibers is very appreciable compared with the actual space existing between the fibers.

Consequently the mass velocity per unit area of cross section is increased as the fluid is deflected into the slit. On the other hand, the liquid which passes around on the opposite sides of the fibers does not change much in velocity since its mass velocity is small compared with the mass velocity of the stream into which it is deflected.

Although it is not essential for the explanation, we shall for simplicity assume that the fluid passes between and around the fibers without head loss due to frictional effects. According to Bernoulli's theorem, the total energy of the system remains constant. Hence, since the mass velocity (kinetic energy) per unit area of cross section increases as the liquid enters the slit, there must be a corresponding decrease in potential energy. This is manifested by a decrease in the static pressure of the liquid in this region. The resultant of these lower pressures in the slits and the higher pressures directly on the opposite sides of each of the fibers moves the fibers toward each other.

It seems reasonable that forces of a similar nature would also be active when a fluid is forced through a fibrous diaphragm. In a diaphragm, with its random arrangement of fibers, lower static pressures should tend to exist in the region between the closer fibers. The resultant of these forces would make the closer fibers move still closer together, thereby increasing the distances between the fibers which were already farther apart. In other words, the larger slits between the fibers would increase in width at the expense of the smaller ones. During these changes the porosity (percentage of void space) would remain the same; no compression of the fibers needs to be postulated. The permeability, however, would be increased, because the frictional resistance to flow of a few large capillaries is less than that of many smaller capillaries of the same total cross-sectional area.

The actual situation in the diaphragm is complicated by the fact that the head loss is not negligible, and consequently the actual mass velocity per unit of cross section is greater in the larger slits. The mass velocity through a large slit, however, would be found to be lower than that through a smaller slit when reduced to the basis of the same slit width according to the Poiseuille equation. In other words, the velocity in the smaller slits tends to be greater in proportion to the slit width, and the static pressure in the smaller slits is lower, in accordance with Bernoulli's theorem.

In flow through cotton cloth a mechanism whereby the larger pores increase at the expense of the smaller pores had been previously suggested by Underwood (59), but he could not offer a satisfactory physical explanation. He regarded the phenomenon as being related to the compressible nature of the fibers. That compressible fibers are not a requirement for this pressure-rate relation is shown by the fact that King (26) found that the rate increased slightly faster than the pressure in flow through a tube packed with wire gauze. According to the explanation just proposed, the only requirement is that the structural units of the diaphragm be somewhat moveable in relation to each other.

The explanation just presented for the disproportionate rate increases on increasing pressure for flow through cellulose diaphragms is applicable also to similar increases in hardwoods containing tyloses or scalariform perforation plates in the vessels.[7]

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[7] In the present study woods with simple perforations and few tyloses were found to give low pressure exponents: cottonwood, buckeye, and silver maple all had pressure exponents close to 1.1 for a reduction of pressure from 5 cm. to 3 cm. of mercury for flow of water through sections 2 cm. thick. Furthermore, after slight variations in the rate of flow at the start of penetration, an almost constant rate was soon reached.

In flow through diaphragms made up of granular materials, this "agglomerating" effect would likewise be present, but other factors might also enter in to cause the disproportionate flow which is observed.

In order to extend this explanation to flow through pit membranes, it is only necessary to postulate that the porous portion of the pit membrane is fibrous in nature. Since the walls of wood fibers have been found to consist of fibrils, a fibrillar conception of the pit membrane would also seem to be quite in order although no specific observations on this point have been brought to the writers' attention. The conception of the pit membrane as a loosely packed diaphragm several fibrils thick would account for the fact that investigators have never been able to find clear cut, direct visual evidence of actual holes extending through the membrane, although the maximum pore radii of most woods (as calculated by Stamm) are within the range of microscopic visibility.

Grondal has enlarged photomicrographs of pit membranes of Douglas fir to a total magnification of 3000 diameters without obtaining definite evidence of actual perforations. In the fibrous diaphragm conception of the pit membrane, the liquid follows a tortuous path in traversing the membrane. One then would not expect to see perforations in the membrane any more than one would expect to see holes straight through a quantitative filter paper.

We can now return to complete the explanation of the time lag which always accompanies a pressure change during penetration. It was pointed out on page 40 that a certain length of time was required for most of the diaphragms studied to come to equilibrium whenever the pressure was altered. According to the interpretation of the pressure-rate relation which has just been presented, a certain time would be required for the fibers or fibrils to shift so that there would be a new equilibrium between the static pressures and the internal stresses which act on these structures. That is, there is one position of the fibers or fibrils which is the equilibrium arrangement when there is no flow.

With increasing pressure gradients static pressure differences which tend to distort the original structure arise so that the fibrous units shift until a new balance between the forces is attained. The movement of one unit will alter the forces on the adjacent unit, hence a certain time is required before the new equilibrium is reached.

2. Flow in the Secondary Direction.[8]—Referring again to the diagrams of Prandtl and Tietjens, we find that if two spheres are suspended a short distance apart, with their line of centers *parallel*[9] to the path of flow, there is a tendency for these spheres to move farther apart. This apparent repulsion between spheres is likewise explained on Bernoulli's principle. The liquid which flows around the first sphere into the region between the spheres suffers a decrease in velocity without corresponding loss in total energy. This loss in kinetic energy is balanced by an increase in potential energy, which is manifested by an increase in the static pressure of the liquid between the spheres. This greater static pressure tends to move the spheres apart.

This reasoning can be extended to apply to flow through cellulose diaphragms as was done in the preceding section. The net effect would be that when a section parallel to the path of flow is considered, the tendency is for the smaller interstices to increase at the expense of the larger due to the differences in the static pressures on opposite sides of the fibers. These forces then tend to keep the fibers apart so that they are separated by somewhat equal distances when viewed perpendicular to the path of flow. Thus any localized force tending to compress the diaphragm would meet with increased resistance as the distance between the fibers became less. This may explain the lack of any noticeable compression of a loosely formed cellulose diaphragm during penetration. There remains, however, the uniform pressure gradient across the entire diaphragm, which should compress the diaphragm if sufficiently high pressure were applied.

This effect is the direct opposite of that previously discussed. It would indeed partly counteract the effect of the increase in the large capillary sizes in the primary direction. However, permeability in the primary direction is a much more important factor than permeability in the secondary direction in determining the mass velocity of flow through the capillaries; permeability in the secondary direction only enters in because of the tortuous path which the liquid follows in traversing the diaphragm. Hence the net effect would still be a disproportionate increase in rate of flow as the pressure is raised.

From these theoretical considerations it was predicted that if rate of flow at a low pressure in one direction through a fibrous diaphragm were measured before and after penetration at a high

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[8] For definition of secondary direction see page 54.

[9] In contrast to the arrangement in the previous discussion, in which the line of centers was perpendicular to the path of flow.

Table 3. A Test of the Rate-Flow Theory

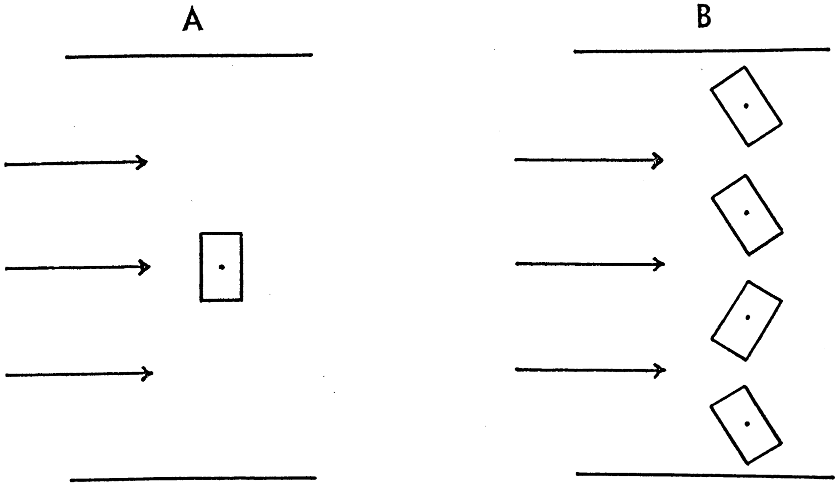
Pressure (cm. of Hg.)	Volume of flow (cc.)	Rate of Flow (cc./min.)		Per cent increase or decrease from previous rate
		Penetration up through cell (primary direction)	Penetration across the cell (through the 5 mm. tubing) (secondary direction)	
10	4	....	0.681	....
10	6	0.366	....	....
100	50	7.41	....	....
10	......	0.453	....	+24
10	......	....	0.635	− 7

Run B-20—Distilled water through loblolly pine springwood unbleached soda pulp. A rubber cell was made by boring a hole 1.7 cm. in diameter through a rubber stopper 2.7 cm. thick. Then a small hole perpendicular to the first was bored in the side of the stopper. Two pieces of glass tubing of 5 mm. internal diameter were inserted through this smaller hole from each side of the stopper and made flush with the inside surface of the stopper. Two wires were then wrapped around the circumference of the stopper, to prevent it from bulging when clamped in the apparatus. One of the glass tubes was connected to the liquid supply, while the other was connected to an arrangement for measuring the rate of flow.

pressure in a direction perpendicular to the first, the rate in the first direction would be found to decrease, while at the same time the rate of flow at the low pressure in the second direction had been increased. The experimental confirmation of this prediction as shown in table 3 provides definite evidence that the explanation of the pressure-rate relation as presented is essentially correct.

C. Proposed Explanation for Decreasing Rates of Flow

We have seen how certain principles of hydraulics, derived from the study of flow of fluids past objects suspended across the path of flow, were useful in interpreting the pressure-rate relations of cellulose diaphragms. The extension of this line of reasoning to softwoods involved a conception of the pit membranes of tracheids as fibrous structures of considerable porosity. Continuing with this method of approach, a simplified large scale model of a wood fiber (a 6-inch length of wood having a rectangular cross section) was fixed in a frame so that it could pivot freely on its longitudinal axis. When this system was drawn through water with the longitudinal axis of the fiber model perpendicular to the path of flow, the fiber always took up such a position that one of its two wider faces was perpendicular to the path of flow. This was the position which offered the maximum resistance to flow. See the following diagram.



The length of the frame was slightly greater than four times the length of one diagonal of the rectangular cross section of the fiber model. This allowed four such fiber models to be placed in parallel positions along the frame, with each fiber still being able to pivot freely on its longitudinal axis. When this frame containing the four fiber models in position was drawn through a large volume of water in the manner previously described, the fiber models then turned until one diagonal of each was perpendicular to the path of flow (Fig. B of the diagram shown above). Since in this position flow through the frame was practically cut off, as only a narrow slit remained between the fibers, this was again the position of maximum resistance to flow. Thus, although the equilibrium orientation of the individual fiber models was different in each case, both positions were those of maximum resistance to flow.

Since cotton and other rag fibers are even more noncylindrical than wood fibers, these observations form the basis for a logical general explanation of the falling off in rate of flow through fibrous materials. In the case of cellulose diaphragms and filter media, this turning of the fibers on their axes so as to offer more resistance to flow does not all take place immediately, for most of the individual fibers are in such close contact with other fibers that motion is for the moment prevented. The restraining forces on some of the fibers, however, are insufficient to prevent their pivoting on their longitudinal axes to some extent, so as to offer more resistance to flow. In so doing they release some of the restraint on contiguous fibers so that they in turn are able to move somewhat, etc.

When a suspension of a long-fibered wood pulp was poured through a tube having a screen over the bottom end, a very loosely constructed mat of fibers was formed. This mat showed a comparatively slight decrease in rate of flow with time. The decrease was possibly due to a situation analogous to A in the diagram on page 59, in which the pore space is relatively large compared with the fiber thickness. With greater degrees of packing the rate of flow decreases more rapidly. The situation then becomes analogous to B in the diagram on page 59 except that the fiber arrangement would be random. With still further packing the diaphragm again gave rates of flow which did not fall off so rapidly. This was because the tight packing of the fibers against each other largely prevented the pivoting action.

A similar pivoting action might take place in the scalariform perforation plates of hardwoods such as paper birch. The bars of the plates are thin ribbon-like structures stretched across the ends of the vessel segments. Apparently, in the vessel as it is first formed, the position of these bars across the path of flow is practically that which offers the greatest resistance to flow. Horticulturists have shown that only the outer few annual rings function in conduction in the living tree. Possibly when the vessels cease to function in conduction the perforation plates dry out partially; as the result, the bars become somewhat twisted so that they are no longer in the positions which offer the maximum resistance to flow. The data of Erickson, Schmitz, and Gortner give no evidence that seasoning results in greater decreases in rate of flow. However, their data give no indication as to what extent a seasoning action may have taken place in the living tree. The penetrated portion of their sections presumably did not involve the last few outer rings of the sapwood. The limited experimentation on penetration of unseasoned paper birch sapwood, which was included in the present study, indicated that the outer region gave very low rates of flow and little decrease in rate of flow. (A section 1 cm. thick of 1.7 square cm. area had an initial permeability of 9 cc. per minute at 100 cm. of mercury. Three matched sections showed 56, 75, and 61 per cent of the initial rate after 16 hours of flow; the rate of flow fell off faster for those sections which had the greater initial rates of flow.)

When penetration is started between the twisted, ribbon-like bars of the perforation plates, there is an even greater tendency than with the fibers of rectangular cross section previously considered for the structures to orient themselves with their wide faces perpendicular to the path of flow. With birch sapwood there is an important difference in the rate of flow curve when plotted as a log-log function of time. For instance, if the data of Erickson, Schmitz, and Gortner (13) for rate of flow of water through paper birch sapwood had been plotted on figure 4 in this manner, the curve would drop more sharply at the start, then tend to flatten out, crossing over all the other curves; apparently a true equilibrium rate was being approached in this case. This is what would be expected because when the bars are in the position of maximum resistance to flow the porosity of the plate is still about 50 per cent or over. The rate of flow would nevertheless have been greatly reduced, as the resistance to flow through the larger slits at the original higher porosity would be much less (since resistance to flow through a slit varies inversely as the cube of the slit width, or since head loss in the slit orifices is directly proportional to the difference between the squares of the average linear velocities through the slits between the bars and that through the main channel of the vessel—depending on the manner in which one wishes to regard the resistance to flow through perforation plates).

With paper birch sapwood, rapid alternations of direction of flow generally produced increases in rate of flow; these increases were proportionately greater than those observed for softwoods. Two possible explanations of this increased rate of flow will be considered: (a) a washing out of particles; and (b) a return toward the position of a mechanical equilibrium.

Explanation (a) was discounted earlier in this work. To this evidence may be added that in penetration of seasoned sections by liquids of high specific gravity (mercury and bromoform) the rate of flow decreased as rapidly when penetration was down as when penetration was up through the wood. If extraneous matter had been present in the vessels, the buoyant action of these liquids should have forced the particles up against the perforation plates, so that rate of flow would have fallen off more rapidly when penetration was up through the wood. Also the comparison of rates of flow through sections of paper birch sapwood which had been evacuated under water and then centrifuged in one of the three structural directions with those of matched control samples gave no conclusive evidence of the presence of particles.

Explanation (b), although hazardous, appears to be the best that can be offered at the present time for this increase in rate of flow through birch produced by rapid alternations of direction of flow. It could be assumed that the drying rate of different surfaces of the perforation plate is very nonuniform, possibly taking place from one side only, so that a condition equivalent to case hardening in woods exists in the bars of the perforation plates. When the wood is resoaked, therefore, the bars do not go back to their former mechanical equilibrium positions, which were also the positions of maximum resistance to flow and are still the positions which they tend to assume during penetration. After a period of penetration, the agitation produced by alternations tends to allow the bars to return to the position in which their internal stresses are a minimum, thus increasing the slit width.

In this investigation the work on paper birch was not of sufficient scope to warrant many general conclusions regarding flow through this wood. It is discussed here only to show that it may be possible to explain the phenomena in flow through this wood on the same basis as used for cellulose mats and softwoods.

In the discussion of the pressure-rate relation the conception of the pit membrane of softwoods as a fibrous structure of considerable porosity was developed. To explain the decreasing rate of flow through such a membrane, it is necessary only to assume that the fibrous elements composing this membrane are not truly circular in cross section. During flow these fibrous elements would pivot so that they offer more resistance to flow. The agitation produced by alternations of direction of flow would tend to make the elements of the pit membrane turn back to their former positions of mechanical equilibrium.

On the basis of the explanations of the flow phenomena which have been put forward in this and the preceding section, it was predicted that constant rate of flow should be obtained through filter media made of wool fibers which have oval cross sections (diameter ratio of 0.8), but are prevented from pivoting by the interlocking felting action of the fiber scales. This was found to be the case in the penetration of several thicknesses of a dense, felted wool cloth. As was also predicted, the rate of flow increased out of proportion to the pressure rise when pressure was increased during penetration. A dense filter fabric woven from an artificial fiber of essentially circular cross section (a vinyl polymer, Vin-17, Wellington-Sears Corp.) also gave almost constant rate of flow, and the previously mentioned pressure-rate relation.

Thus the characteristic pressure-rate relation, which was investigated in this work only because it appeared to be inseparably tied up with decreasing rate of flow, now appears to be rather an independent phenomenon. The two are related only in that they require that the structural elements of the membrane be somewhat moveable. By the pressure-rate relation it should be possible to distinguish between a brush-heap and an open pore system in other membranes of unknown sub-microscopic structure.

A possible objection to the proposed explanation of decreasing rates of flow is that benzol and 95 per cent ethanol gave constant rate through filter paper and much less decrease in rate of flow through woods than did water. Also, the much smaller percentage decrease in rate of flow of salt solutions through wood as compared with similar data for distilled water needs explanation. The larger effective pore size when salt solutions are used, due to the decreased thickness of the electrical double layer, would in part at least account for the relatively smaller decreases in rate of flow with salt solutions, for the same degree of pivoting of a fibrous element would cause a relatively smaller decrease in pore size when salts are present. Possibly the benzol and alcohol tend to immobilize the cellulose fibers. Cellulose is certainly embrittled in both alcohol and benzene so that the nonsolvated fibers might be expected to be essentially rigid. Since the fibers are not swollen by these media the effective pore size should be greater and, at least in the case of benzol, the double layer thickness should be greatly reduced. The low pressure exponents when balsam fir and eastern hemlock sapwoods, which ordinarily have high pressure exponents, were penetrated by $HgCl_2$ solution indicated also an immobility of the fibrous units when the woods were penetrated by the 0.01 N salt solution. Here again the coagulating and dehydrating effect of mercuric ions on hydrophilic-gels is offered as a probable explanation.

The decreasing rates of flow of ethanol (Fig. 8) and benzol (13) through woods as compared with the constant rates of these liquids through filter paper indicate either that the pit membrane does not consist of cellulose alone, or that other factors besides the pivoting of the fibrils are active in producing the decreasing rate of flow.

Proposed Structure of the Pit Membrane.—In order to interpret the phenomena observed, the pit membrane is best regarded as consisting of a relatively impermeable disk-shaped torus which is suspended by fiber-like structures radiating out from its edges and attached to the primary cell wall proper. These structures may indeed be continuations of similar fibrillar elements existing in this cell wall. These fiber-like strands are not circular in cross section. The difference between their maximum and minimum cross-sectional dimensions is of the same order of magnitude as the distance between individual strands. The porous area of the membrane is composed of several of these fiber-like strands in thickness. These strands may or may not be arranged in definite layers. In penetration at high pressures it is possible that the forces of static pressure which are active cause the strands to arrange themselves so that large (microscopic) slits straight through the membrane do actually exist temporarily.

This conception of the pit membrane makes it somewhat similar in structure to a loosely packed cellulose diaphragm, yet it differs in two respects. In the cellulose diaphragm the fibers are randomly arranged and each fiber is in contact with other fibers at several points. In the structure proposed for the pit membrane, adjacent fibrils are practically parallel, and are held somewhat apart from each other by their different points of attachment to the primary wall.

An alternative view is that the pit membrane, since it is part of the primary cell wall, is likewise composed of laterally wrapped fibrils of cellulose instead of the radiating arrangement which has been postulated to conform to the observations of I. W. Bailey (1). The phenomena in softwood penetration can be explained equally well with either arrangement.

Evidence of interpenetrating systems of lignin and cellulose in the cell walls has been found by several workers (Ritter; Kerr and Bailey; Harlow). The relative absence of one of these constituents (probably the lignin) from the pit membrane could account for the high permeability in this region. Possibly this missing constituent has been compressed into the torus; this hypothesis[10] would account both for its lack of permeability and its greater thickness.

SUMMARY OF PART II

The disproportionate increase in rate of flow through woods and diaphragms composed of cellulosic fibers or granular particles has been explained by the application of Bernoulli's theorem

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[10] The explanations set forth in sections B and C of Part II were formulated after the bulk of the data had been collected. Only three runs were made with these points of view in mind. Although the results of these runs were as predicted, it would have been desirable if more time had been available in which to have performed a few more well directed experiments. Admittedly, a great deal of theorizing based only on indirect evidence has been indulged in in these sections. It is hoped, however, that these speculations may persuade others more skilled in micro-manipulative, micro-chemical, and photomicrographic techniques to seek confirmation or refutation of these ideas from more direct evidence.

to the determination of the relative static pressures on different sides of the individual units composing the diaphragms. From these theoretical considerations it was shown that the larger capillaries would increase at the expense of the smaller ones, resulting in increased specific permeability at higher pressures.

Both by theory and experiment it has been shown that the specific permeability in a direction perpendicular to the main path of flow through a diaphragm tends to be decreased by an increase in pressure which simultaneously increases the specific permeability in the primary direction.

The decrease in rate of flow through cellulose diaphragms is brought about by a pivoting of the fibers on their longitudinal axis in such a manner that they offer a greater resistance to flow. The torques produced by motion of the liquid around fibers suspended across the path of flow are in equilibrium only when the orientation of the fibers is that which presents the greatest resistance to flow. The decrease in rate of flow through woods probably is largely due to a similar action in the structural units of the membrane.

When pressure is first applied to a wood section or cellulose diaphragm, two forces are active on its structural units: (a) the resultant of the unequal static pressures on the fibrous elements, which tends to increase rate of flow; and (b) the resultant of the torques on these units, which tends to decrease the rate of flow. During the first few minutes either of these may be dominant, so rate of flow may either increase or decrease. The forces of (a) reach equilibrium rapidly; with further penetration only the forces of (b) are active, so rate of flow always decreases.

When the logarithm of the rate of flow is plotted against the logarithm of the time of penetration, a rather straight line results after the forces of (a) have come to equilibrium. As long as our experiments were run (up to 30 hours in some cases), there was no evidence that an equilibrium of other than zero rate of flow was being approached in most softwoods or in cellulose diaphragms of not too loose structure.

The hypotheses developed in this section have been used successfully for the prediction of phenomena in flow through other materials.

CONCLUSIONS

1. A pivoting action whereby the fibrous units assume positions which offer greater resistance to flow is suggested as the cause of the decreasing rate of flow through cellulosic filter materials.

2. Probably this same mechanism also is active in producing the falling off in rate of flow through woods.

3. The disproportionate increase in rate of flow when pressure is increased in penetration of these materials has been attributed to a lateral movement of the fibrous units, brought about by differences in the static pressures of the liquid on opposite sides of the fibrous units, whereby the larger capillaries are increased at the expense of the smaller ones.

4. A bulging of the pit membrane does not need to be postulated in explaining any of the phenomena observed. Such a supposition cannot adequately account for the pressure-rate relation.

5. Electrokinetic changes, swelling, plugging by particles, blocking by air, and pit aspiration have been eliminated as important factors in producing decreasing rate of flow.

6. Electrokinetic properties are, however, factors comparable with viscosity in importance in determining rate of flow in very small capillaries.

7. The pores of softwoods are below the critical radius above which the common streaming potential equation holds. The zeta potential when calculated from this equation appears to decrease with time of penetration.

8. The higher rates of flow with salt solutions are probably the result of the decreased thickness of the electrokinetic double layer.

9. The percentage increase in rate of flow when the electrolyte content of the penetrating liquid is increased is inversely related to the size of the capillary. This fact could be the basis for an additional method of estimating the size of submicroscopic pores.

10. Rapid alternations of direction of flow on diaphragms through which rate of flow has decreased (as a result of penetration in both directions) generally results in an increased rate of flow in both directions.

11. "Spurts" in one direction only have the same effect as alternations of direction, but to a lesser degree.

12. Less frequent alternations of direction of flow at the same pressure (allowing an appreciable volume—about 15 cc.—to flow in each direction) have the opposite effect, causing the rate of flow to decrease more rapidly than if an equal volume of liquid had been passed through the wood or cellulose diaphragm in one direction only.

13. After a wood section has been penetrated in one direction for some time, a very different (usually higher) rate of flow may be observed when the direction of flow is reversed.

14. No equilibrium rate (other than zero) is approached in penetration of softwoods.

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